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Soybean growth responses and soil chemical changes resulting from applications of pyrite recovered from Iowa coal

by

James Delbert Kaap

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INTRODUCTION

The current energy crisis has stimulated interest in mining and consumption of Midwestern coal. Much of the coal in this area contains a high level of S which is emitted into the atmosphere upon burning. Air pollution control regulations will require the processing of such coal to reduce the content of iron pyrite (FeS_2) and other S-bearing impurities before it can be utilized.

Disposition of pyritic materials resulting from mining and processing operations poses some problems. They must be handled in a manner to insure that the acidic decomposition products do not damage vegetation or contaminate drainage water from the area. In most mining operations, these waste materials are buried in order to minimize any potential damage.

Despite these problems, the chemical composition of pyrite suggests that it might have some value for controlled use as a soil amendment to correct excessive alkalinity and to supply Fe and S. One area where such materials might have some value is on the calcareous soils in the Clarion-Webster association in north-central Iowa and south-central Minnesota. It is estimated that Fe deficiency may reduce soybean yields on as many as one-half million acres annually in this area. Foliar sprays of various Fe compounds recommended as a corrective measure at the present time are not widely used, and an economical, effective soil additive would be of value.

The objective of this series of laboratory and growth chamber experiments was to obtain some information regarding the potential value of

waste pyrite as a source of Fe for soybeans. Objectives of specific experiments were:

(1) To determine in the laboratory whether the pyrite contained or produced substances known to be toxic to plants.

(2) To determine in an incubation study the beneficial and adverse effects of pyrite and elemental S on soil acidity and levels of plant-available Fe, Mn, and Zn in selected Iowa soils.

(3) To compare the foliar and growth response of an Fe inefficient soybean cultivar grown on selected Iowa soils treated with pyrite or elemental S under growth chamber conditions.

LITERATURE REVIEW

Source and Oxidation Reactions of Pyrite

The current energy crises will promote coal mining and consumption. Iowa coal contains as much as 9% S, most of which is in the form of iron pyrite (Energy and Mineral Resources Research Institute, 1977; Gulliford and Sendlien, 1978). Recent government air pollution regulations will require that much of the coal be processed to remove the acid-forming pyritic material before it can be burned (Energy and Mineral Resources Research Institute, 1977). Disposal of waste materials that contain pyrite is a costly problem since pyrite is potentially hazardous to the environment. Upon oxidation, pyrite releases sulfuric acid and iron sulfate. This first step can be written according to the following (1) chemical reaction (Leuthen et al., 1953; Temple and Delchamps, 1953).

$$FeS_2 + \frac{7}{2} O_2 + H_2O \rightarrow Fe^{++} + 2SO_4^{=} + 2H^{+} \quad (1)$$

The ferrous (Fe^{++}) iron can further oxidize to ferric (Fe^{+++}) iron according to the following (2) overall reaction (Stumm and Morgan, 1970).

$$2\ FeS_2 + 7\tfrac{1}{2}\ O_2 + 7\ H_2O \rightarrow 2\ Fe(OH)_3 + 8\ H^{+} + 4\ SO_4^{=} \quad (2)$$

The resulting compounds can be major sources of stream pollution. Not surprisingly, soils developed from parent materials high in pyrite can become acidic. Poor plant growth on oxidized pyritic mine spoils and so-called acid sulfate soils, which are especially widespread in the Netherlands and in the coastal plains of the tropics, is attributed mainly to the release of toxic concentrations of aluminum, manganese, and other dissolved metals from these soils as a result of extremely

high acidity (Barnhisel and Massey, 1969; Cate and Sukhai, 1964).

Agricultural Applications of Pyrite

Agricultural uses of pyrite have been investigated in the past, mainly as a source of sulfur for S deficient soils (Odelien, 1967; Banath, 1969; Barrow, 1971; Metson et al., 1971), and as an acidifier to improve the structure of sodic soils (Smith, 1930; McGeorge and Breazeale, 1955). Molina Abella (1967) used iron pyrite to acidify calcareous soils to bring more phosphate into solution. More recently a number of workers have studied iron pyrite and pyritic materials as a source of Fe in calcareous, Fe deficient soils (Barrau and Berg, 1977; Fuller and Lanspa, 1975; Wallace et al., 1976a; Vlek and Lindsay, 1978).

Earlier work has shown pyrite oxidation in soils to be a sluggish process, thus limiting its usefulness as a soil conditioner (Smith, 1930; McGeorge and Breazeale, 1955). More recent studies have shown that the reactivity and effectiveness of mined pyrite as a source of sulfur and plant-available Fe greatly increases with decreasing particle size (Banath, 1969; Banath and Holland, 1976; Vlek and Lindsay, 1978). Clay-sized particles applied at a rate of 1% S as FeS_2 and incubated for one month followed by a second 1% S as FeS_2 application decreased the pH of a calcareous loamy sand from 8.3 to 7.8 after the first month and to 5.7 after two months (Vlek and Lindsay, 1978). The DTPA-extractable Fe increased from 1.5 to 64 ppm for the clay-sized pyrite treatment during the first month while Cu doubled and Mn

quadrupled. These investigators concluded that the increased availability of Fe was a direct result of pyrite oxidation as shown by equation (1). The Fe^{++} is further oxidized to Fe^{+++} and is readily precipitated to ferric-hydroxides as shown in equation (2). The release of available Fe from pyrite depends on the rates of pyrite oxidation and ferric hydroxide precipitation. Other factors which affect pyrite oxidation include O_2 level, elemental S, soil pH, microorganisms, moisture, level of P in the soil, and crystalline structure of pyrite (Barrau and Berg, 1977).

Environmental Factors Influencing Iron Chlorosis

Iron chlorosis in plants is a very complicated phenomenon. Wallace and Lunt (1960) listed 14 environmental factors which may contribute to Fe chlorosis including: (1) low supply of Fe in the soil, (2) amount of calcium carbonate in the soil, (3) high concentration of bicarbonate in the soil or irrigation water, (4) over-irrigation or high water conditions, (5) high phosphate conditions, (6) high levels of other metals such as manganese, copper and zinc, (7) low temperatures, (8) high temperatures, (9) high levels of nitrate nitrogen, (10) unbalanced cation ratios, (11) poor aeration, (12) certain organic matter additions to the soil, (13) viruses, and (14) root damage by nematodes. Not only are many factors involved, but often they interact with each other as well as the physiological properties of a plant. Plant species, as well as cultivars within a species, can greatly differ in their ability to absorb Fe from soils (Brown et al., 1972). Soil and management factors

can modify the nature and extent of root system and significantly affect the Fe uptake within the same cultivar (Wallihan and Garber, 1968).

Further, temporary unfavorable soil conditions may induce the development of Fe deficient plant tissues which can persist after the causative condition has disappeared. At best, chemical soil tests can estimate only a few of these parameters such as low supply of Fe in the soils or pH. Therefore, except under carefully controlled conditions, precise predictions of Fe deficient soils cannot be expected.

DTPA Soil Test

Because of the importance of complexed, chelated, and adsorbed Fe, Mn, and Zn to the pool of these available micronutrients, chelating agents are frequently successful as micronutrient metal extractants. Chelating agents extract a large portion of this pool with a minimum of less available forms. The amount of chelated metals that accumulates in solution depends on the activity of the metal ions in the soil (intensity factor) and the ability of the soil to replenish those ions (capacity factor). One such chelating agent used as a metal extractant is diethylene triaminepentaacetic acid (DTPA). Lindsay and Norvell (1978) developed a DTPA soil test to determine levels of Fe, Zn, Mn, and Cu in near-neutral and calcareous soils of Colorado. They correlated DTPA-extractable Fe, Zn, and Mn from 77 soils to the response of corn to Fe, Zn, and Mn fertilizers in the greenhouse. They obtained critical nutrient levels of 4.5 ppm for Fe, 0.8 ppm for Zn and a tentative 1.0 ppm for Mn. The buffered extractant contains DTPA,

triethanolamine (TEA), and $CaCl_2$ and the pH is adjusted to 7.3 where Zn-DTPA and Fe-DTPA are stable. At pH's above 7.3, the amount of Fe extracted decreases rapidly even though the amount of Zn extracted remains high. Some potential for chelation of Mn by DTPA exists at pH 7.3 under oxidizing conditions, but it is more difficult to predict since it is redox dependent (Norvell and Lindsay, 1972).

Calcium chloride is included in the extractant to inhibit the dissolution of $CaCO_3$ in calcareous soils which releases occluded micronutrients that are normally unavailable for absorption by roots (Norvell and Lindsay, 1978). Also, when $CaCO_3$ dissolves, Ca competes with the micronutrients for complexing sites of the chelates. The TEA buffers the extractant at pH 7.3 and burns cleanly during flame atomization in atomic absorption spectrophometry when the metals are measured.

de Boer and Reisenaur (1973) used a critical level of 6 ppm of DTPA-extractable Fe to predict successfully Fe deficiency of field-grown sorghum at 11 of 13 locations in California. In the greenhouse a critical level of 5 ppm of DTPA-extractable Fe was used successfully to predict sorghum response in 13 out of 14 soils.

Using a critical level of 0.5 ppm of DTPA-extractable Zn, Brown et al. (1971) examined 92 California soils and found the DTPA soil test identified 83% of the soils which showed a plant response to Zn fertilization. Gogan (1975) found that DTPA-extractable Zn showed the best correlations between soil Zn and corn yield response among five soil test procedures, particularly on calcareous soils. Randall et al. (1976) concluded that DTPA could successfully determine available Mn in

low organic matter soils (<6%).

After adding labeled ^{65}Zn to 30 soils, Lauer (1971) found that corn plants and the DTPA extractant removed Zn from the same soil labile pool (r^2 = 0.97). The soil labile pool is defined by Rule and Graham (1976) as "the amount of an element (X) in the soil solution and solid phase as measured by chemical equilibrium or plant uptake, utilizing isotopic exchange, which becomes available for plant uptake during the growing season." Other data show that micronutrient metals from labile pools of these metals in soils are extracted by DTPA (Wallace and Mueller, 1968; Lopez and Graham, 1972; Rule and Graham, 1976).

Sample preparation and extraction procedures must be standardized to obtain meaningful soil test levels (Soltanpour et al., 1976). Standard procedures are particularly important for Fe where a critical level of 4.5 ppm of DTPA-extractable Fe may be equivalent to 0.01% of the total Fe in soils.

DTPA-Extractable Metals from Air-Dry and Moist Soils

A number of reports show that the DTPA-extractable Fe, Zn, and Mn contents from moist soils are significantly lower than from air-dry soils. In his study of 23 Iowa soil types including Canisteo, Harps and Webster soils, Gogan (1975) found that DTPA extracts from field-moist samples contained 39% less Zn, 31% less Fe, and 25% less Mn than extracts from air-dry samples. Although air-drying greatly affected extractable Zn, the Zn levels of air-dry and field-moist soils both correlated equally well to corn dry matter yields in the greenhouse. Khan

and Soltanpour (1978) reported a significant decrease of 50% in DTPA-extractable Fe and Mn in calcareous soils incubated at 1/3 bar moisture tension for 1 week. Air-drying these soils after incubation increased the extractable Fe content to near original levels. Oven-drying increased the levels of DTPA-extractable Fe, Mn, and Zn 2 to 6 fold. Khan and Banwart (1979) incubated 20 soils ranging in pH from 4.2 to 9.4 at field-moisture capacity for 1 week and confirmed the observation of Gogan (1975) that moist incubation decreases DTPA-extractable Fe and Zn in acid as well as alkaline soils. They also found that the addition of toluene reduced microbial CO_2 evolution by 90% in moist-incubated soils but did not affect the decrease in extractable Fe and Zn. They suggested that fixation of available Fe and Zn in moist-incubated soils is nonmicrobial in nature. The correlations between air-dry and moist samples for Fe and Zn were highly significant ($r = 0.89$ and $r = 0.99$, respectively). By using regression equations, if soils are analyzed air-dry, the values can be corrected to a soil-moist basis.

A number of studies have shown that Fe chlorosis of plants has been associated with relatively moist soil conditions (Burtch et al., 1948; Elgala and Maier, 1964; Lindsay and Thorne, 1954; Mortvedt, 1975; Mortvedt et al., 1977; Olomn and Racz, 1974; Wallace et al., 1976b; Wallihan and Garber, 1968). Zinc chlorosis in beans growing in relatively moist soils has been observed (Khan and Soltanpour, 1978). Since studies with moist-incubated soils have resulted in decreased DTPA-extractable Fe and Zn (Gogan, 1975; Khan and Soltanpour, 1978; Khan and Banwart, 1979), prolonged wetting under field conditions could reduce Fe

and Zn availability to plants and favor Fe chlorosis.

Excess water in calcareous soils can produce reducing conditions which would favor Fe^{++} formation in the soil. Fe^{++} is available for plant uptake. However, excess water also causes poor soil aeration and results in a lack of oxygen to plants which inhibits active Fe uptake by the roots (Lucas and Knezek, 1972). Low oxygen tension of high-moisture soils reduced the root system of orange seedlings, thus reducing their Fe uptake (Wallihan, 1961; Wallihan and Garber, 1968).

Another possible explanation has been offered. In India, Takker (1969) found that Fe^{+++} persisted for 35 days in waterlogged calcareous soils containing low amounts of organic matter. In most other soils, Fe^{+++} was converted to Fe^{++} after 7 days. The slow release of Fe^{++} in calcareous soils may be due to the highly crystalline forms of Fe oxides which very slowly dissolve into available forms. These observations agree with those of Kumada and Asamii (1958) who found that the rate of Fe formation depends on the nature and amount of free Fe compounds, the soil pH, and the organic content of the soil.

High moisture contents of soils also can favor increases in bicarbonate concentration, which can aggravate Fe chlorosis (Porter and Thorne, 1955).

Iron Deficient Soils in Iowa

High-lime soils within the Clarion-Webster soil association of north-central Iowa and south-central Minnesota are often associated with Fe deficiency in soybeans resulting in decreased yields (de Mooy,

1972). In a field survey to assess the levels of available Fe and Zn in high-lime Canisteo and Harps soils of the north-central region of Iowa, Gogan (1975) found that the DTPA-extractable Fe content of 39% of the 82 samples tested were marginal or deficient. The mean pH value of these soils was 8.0 with some pH values as high as 8.4. Chemically, a pH below 5.0 favors Fe^{++} while a pH above 6.0 favors Fe^{+++}. The solubility of Fe^{++} and Fe^{+++} decreases by factors of 10^2 and 10^3 respectively for each unit increase in pH between 4 and 9 (Lindsay, 1972). In studies using Fe chelates, Chaney et al. (1972) reported that soybeans must reduce Fe^{+++} to Fe^{++} before it can be absorbed. It is not surprising that Fe inefficient soybeans, which have difficulty reducing low concentrations of Fe^{+++} to Fe^{++}, often became chlorotic under high-lime conditions. As many as 500,000 acres of soybeans a year may be affected (de Mooy, 1972). Spray treatments with $FeSO_4$ or Fe chelates are recommended to correct the deficiency, but usually more than one application may be required (de Mooy, 1972; Kaap, 1973). Soil applications of inorganic Fe salts require very high rates to be effective (Withee and Carlson, 1959) and are usually uneconomical (Mortvedt and Giordano (1971). Soil-applied Fe chelates can also correct or prevent Fe chlorosis but the material is expensive and may decompose within 1 or 2 years (Barrau and Berg, 1977). Soil-applied pyrite may prove to be an effective alternative over longer periods of time.

Plant Responses to Pyrite

In recent glass house studies, the disposal of large quantities of

waste pyrite and pyrite tailings as soil amendments to correct Fe deficiency in calcareous soil was examined. At the extremely high rates of 45 and 135 metric ton/ha, Barrau and Berg (1977) found that these materials were as effective as conventional iron sources such as $Fe_2(SO_4)_3$ and chelated iron. The pyrite treatments corrected Fe chlorosis in sudangrass (Sorghum vulgare sudanese) and increased yields 160% for the low application rates and 200% for the high rates compared to the control. After the sixth harvest, all pyrite treatments increased plant available Fe 50% to 100% as measured by DTPA extraction. The levels of DTPA-extractable Zn and Mn remained the same or decreased slightly. They suggested that lower rates of application might be adequate if the pyritic materials were ground finer than the 0.1 mm sized particles which were used in this study.

Wallace et al. (1976a) applied waste pyrite containing 45% S at a rate equivalent to 400 metric ton/ha to a highly calcareous (10% $CaCO_3$) soil. This treatment overcame Fe chlorosis in Fe-inefficient PI-54619-5-1 soybeans (Glycine Max L.) and increased dry matter yields 170% compared to the control. The soil pH dropped only slightly (from 7.9 to 7.5) and no heavy metal toxicities were noted. Pyrite applied in a band at rates equivalent to 40 metric ton/ha also overcame Fe deficiency. Pyrite produced acidity in noncalcareous soil (initial pH, 6.2; final pH, 4.1) and inhibited plant growth, probably as a result of Mn and Zn toxicities.

Fuller and Lanspa (1975) found that treating mine tailing material (30% FeS_2) with concentrated H_2SO_4 increased its effectiveness many fold

as a source of Fe. Such acid-treated pyrite corrected lime induced Fe chlorosis and stimulated top growth of two sorghum cultivars.

Plant Response to Elemental Sulfur

Some data have shown that low to moderate levels of elemental S have prevented Fe chlorosis of certain crops grown on alkaline soils. In a field study, Singh (1970) reported that 250 kg/ha of elemental S applied to a calcareous (0.3% $CaCO_3$; pH 8.4) soil prevented symptoms of Fe chlorosis in peas (Pisum sativum L. 'Bonneville') and doubled grain yield compared to the control. Subsequent field experiments showed that foliar sprays of 0.1% H_2SO_4 and $FeSO_4$ were as effective as the elemental S treatment in increasing yields and preventing Fe chlorosis while a foliar spray of 0.1% ferric ethylenediamine di(o-hydroxyacetic) acid (FeEDDHA), an Fe chelate, was ineffective (Bansal and Singh, 1975). They concluded that a low supply of active S in the plant was responsible for the chlorosis, and an increased supply of S increased the physiological availability of Fe as well. In a glasshouse experiment with two Fe sensitive sorghum cultivars, Fuller and Lanspa (1975) obtained a 15% dry matter yield increase with as little as 100 kg S/ha of elemental S applied to a calcareous (3% lime; pH 7.6) soil. Other S treatments included elemental S at rates of 0, 400, 800, 1,600 and 2,000 kg S/ha, and ferrous sulfate at 2,000 kg S/ha. The elemental S treatments at 1,600 and 2,000 kg S/ha increased dry matter yields 7% and 19%, respectively, over the ferrous sulfate treatment. The growth response was not attributed to alleviating N, P, K, Mn, Cu or S deficiencies

in the soil. They suggested that the growth response was correlated with Fe and other factor(s) associated with acidification during oxidation of elemental S. The increase in growth was only partially due to increased Fe availability. In north-central Iowa, elemental S has been applied at rates up to 56 kg/ha to correct Fe chlorosis of susceptible soybeans (R. D. Voss, extension agronomist, Iowa State University, personal communication). No data have been obtained to determine the effectiveness of elemental S treatments.

PART I. POTENTIAL OF SOIL-APPLIED COAL-PROCESSING WASTES TO CAUSE TOXICITIES IN IOWA SOILS

INTRODUCTION

Beneficial or deleterious effects may result from soil applications of waste pyrite. Beneficial effects may include increased levels of plant-available Fe and S upon the oxidation of pyrite (Barrau and Berg, 1977; Barrow, 1971). Pyrite oxidation releases Fe sulfate and sulfuric acid. Applications of pyrite to soil low in free $CaCO_3$ may cause them to become acidic. Other deleterious effects may occur if waste pyrite contains sufficiently high levels of certain elements such as As, Pb, and Se, which are harmful to plants or the animals that ingest them. In addition certain oxidation products of pyrite such as thiosulfate and tetrathionate (Temple and Delchamps, 1953; Gleen and Quastel, 1953) also may be toxic to plants.

In preliminary studies, as much as 300 ppm tetrathionate ($S_4O_6^{=}$-S) sulfur and 70 ppm thiosulfate ($S_2O_3^{=}$-S) sulfur were detected in Iowa coal mine shales and shale-soil mixtures that contained pyrite. Wolkoff and Larose (1975) reported that oxidation of pyrite from tailings resulted in concentrations of thiosulfate as high as 600 ppm in tailing-pond effluents. Under certain microbiological conditions, tetrathionate is oxidized to thiosulfate (Starkey, 1966; Aleem, 1975). Thiosulfate at concentrations of 500-5000 ppm has been found to inhibit root growth and seed germination in several plant species (Audus and Quastel, 1947).

To determine if soil applications of waste pyrite presented any potential harmful effects on plants or animals, these materials were first analyzed for toxic elements. Secondly, an incubation study was

undertaken to determine soil pH and the level of tetrathionate and thiosulfate released after waste pyrite had been applied to four Iowa soils.

MATERIALS AND METHODS

Iron Pyrite

Waste pyrite originating from coal was collected at the Iowa State University experimental coal preparation plant. The pyrite was ground to pass through a 100-mesh screen and analyzed at the Ames Laboratory, Iowa State University, Ames, Iowa. The material was analyzed for pyritic S, total Fe, and total S by the American Standard Testing Methods (ASTM, 1975, 1977). Zinc content of the waste pyrite was measured by atomic absorption determination of the digests prepared for total Fe analysis. The concentration of As, Pb, and Se was determined by emission spectroscopy according to the procedures outlined by Giauque et al. (1973).

Soils

Four soils from north-central Iowa chosen for the incubation study included Canisteo, Harps, Storden, and Webster. Many of the higher-yielding soybean cultivars are especially susceptible to "lime induced" Fe deficiency when grown on the calcareous Canisteo and Harps soils. Applications of pyrite on such soils may prevent or correct symptoms of Fe deficiency in soybeans. The other soils were employed in this study because all four soils may occur together and would receive significant applications of waste pyrite if it is applied as a broadcast field treatment.

Some chemical and physical properties of each soil are listed in

Table 1. The pH, organic matter content, available P, available K, soluble sulfate, and diethylenetriaminepentaacetic acid (DTPA)-extractable Zn measurements were performed at the Iowa State University Soil Testing Laboratory according to the procedures described by Eik (1973, 1977). Inorganic C was determined by the method of Bundy and Bremner (1972). Organic C was determined by the method of Mebius (1960). The particle size distribution was determined by the pipette procedure described by Kilmer and Alexander (1949). Before incubation, the surface (0-15 cm) horizon of each soil was ground to pass through a 2-mm sieve and air-dried.

Reagents

Lithium chloride (0.2 M)--8.4 g of LiCl was dissolved in about 800 ml of deionized water, and the volume was adjusted to 1 liter.

Thiosulfate stock solution--3.871 g of $Na_2S_2O_3 \cdot 5H_2O$ was dissolved in about 800 ml deionized water, and the volume was adjusted to 1 liter. One ml of this solution contained 1 mg S.

Procedure

A 20-g sample of each soil was weighed out into an 8-oz French square bottle and treated with appropriate amounts of waste pyrite. The amount of material applied was based on its S content. The following treatments were used for each soil type: Canisteo--0, 50, 100, 150 µg S/g soil; Harps--0, 50, 100, 150, 200, 400, 600, 800, 1000 µg S/g soil; Storden--0, 50, 100, 150 µg S/g soil; and Webster--0, 50, 100, 150 µg

Table 1. Analyses of four soils from north-central Iowa

Soil series	pH	Organic carbon	Inorganic carbon	Clay	Silt	Sand	Soil test values			
							P	K	S	Zn
		%					kg/ha		ppm	
Canisteo 1	7.8	3.8	0.19	25	45	30	45	115	2.0	1.7
Harps 1	8.2	2.5	1.07	22	31	47	4	57	2.0	1.1
Storden sl	8.3	1.4	0.34	19	28	53	123	233	2.0	0.4
Webster 1	6.5	2.8	0.00	18	39	43	40	244	2.0	2.0

S/g soil. Additional high rates of waste pyrite were applied to the highly calcareous Harps soil because Fe deficiency often is severe in sensitive soybeans grown on this soil. The waste pyrite was thoroughly mixed with the soil. Each pyrite-treated soil was subjected to two levels of water content. Either 5 ml or 10 ml of water was added to the bottles to bring the soil moisture content to about 50% or 100% of the water-holding capacity, respectively. The bottle was stoppered and incubated at 25°C for 14, 28, or 42 days. All experiments were performed in duplicate. Controls were similarly treated but contained no added pyrite. Extractions were carried out at intervals of 14, 28, or 42 days. The bottles were aerated every three days to insure an adequate supply of oxygen.

After incubation, 50 ml of water was added to the bottle, and the contents were thoroughly mixed (1:2.5; soil:water ratio). After 30 minutes, pH was measured by using a glass electrode. Then 50 ml of 0.2 M LiCl was added (final concentration: 0.1 M LiCl), the bottle was shaken for 30 minutes on a reciprocal shaker, and the suspension was filtered through Whatman #42 filter paper. Remaining colloidal material in the extract was removed by refiltering the filtrate through a 0.2-μ Metrical GA-8 membrane filter (Gelman Instrument Co.).

The soil extract obtained was analyzed for thiosulfate + tetrathionate)-S by the method of Nor and Tabatabai (1976). The results were expressed in μg of $(S_2O_3^{=} + S_4O_6^{=})$-S/g of soil.

RESULTS AND DISCUSSION

The chemical analysis of the waste pyrite is given in Table 2. Virtually all its S content, 31.3%, is in the pyritic form. Fe and Zn contents were 34.7% and 0.3%, respectively. Although the amount of Pb in the pyritic waste is many times higher than that of As and Se, Pb buildup in plants is unlikely (Table 2). First, soils are likely to be amended with only a relatively small amount of pyritic waste on a weight-to-weight basis. Secondly, alkaline soils amended with waste pyrite will tend to insolubilize Pb and As and reduce their uptake by plants (Lagerwerff, 1972; Stewart and Smith, 1922). The low Se content of pyrite is unlikely to accumulate in plants to levels of 4-5 μg Se/g, which are considered toxic to animals (Kubota and Allaway, 1972). The results of the analysis suggest that there would be little, if any, danger of toxic levels of these compounds after applications of pyrite on the four soils, especially on calcareous soils.

The results of the incubation experiment involving pyrite-amended Iowa soils show that thiosulfate and tetrathionate were not detected in the LiCl extracts (Table 3). This result suggests that inasmuch as pyrite oxidizes in soil, little, if any, tetrathionate and thiosulfate formation or buildup can be expected 14 days after application. Therefore, seed germination and root growth should not be affected by these two sulfur compounds in soils treated with Iowa pyrite. The pyrite treatments decreased the pH of the four soils no more than 0.4 of a pH unit regardless of incubation period (Table 3). Harps soil amended with 1000 μg S as pyrite, after 42 days incubation, exhibited the largest change in

Table 2. Analyses of waste pyrite recovered from the Iowa State University experimental coal preparation plant

Element	Quality present
S as FeS_2	31.3%
Total S	31.3%
Total Fe	34.7%
Total Zn	0.3%
Total As	1.3 µg As/g
Total Pb	96 µg Pb/g
Total Se	0.2 µg Se/g

Table 3. Effect of pyrite S on soil pH and (tetrathionate + thiosulfate)-S after 3 periods of incubation at 25°C

Pyrite S treatment	Soil water content	pH			$S_4O_6^{=}$-S + $S_2O_3^{=}$-S		
		14[a]	28[a]	42[a]	14[a]	28[a]	42[a]
µg/g soil	% WHC[b]				µg/g soil		
		Canisteo 1					
0	50	7.7	7.6	7.5	0	0	0
0	100	7.7	7.6	7.5	0	0	0
50	50	7.7	7.6	7.7	0	0	0
50	100	7.7	7.6	7.5	0	0	0
100	50	7.8	7.7	7.7	0	0	0
100	100	7.7	7.6	7.7	0	0	0
150	50	7.8	7.7	7.6	0	0	0
150	100	7.7	7.7	7.6	0	0	0
		Harps 1					
0	50	8.4	8.2	8.5	0	0	0
0	100	8.3	8.0	8.4	0	0	0
50	50	8.3	8.2	8.2	0	0	0
50	100	8.3	8.1	8.3	0	0	0
100	50	8.4	8.3	8.5	0	0	0
100	100	8.3	8.2	8.4	0	0	0
150	50	8.3	8.3	8.3	0	0	0
150	100	8.4	8.3	8.3	0	0	0
200	50	8.5	8.3	8.4	0	0	0
200	100	8.3	8.2	8.1	0	0	0
400	50	8.3	8.3	8.5	0	0	0
400	100	8.3	7.9	8.3	0	0	0
600	50	8.2	7.9	8.0	0	0	0
600	100	8.1	7.8	8.1	0	0	0
800	50	8.1	8.1	8.3	0	0	0
800	100	7.9	7.9	8.3	0	0	0
1000	50	8.1	8.1	8.1	0	0	0
1000	100	7.9	7.8	8.1	0	0	0

[a]Incubation time in days.

[b]Percent water-holding capacity.

Table 3 (continued)

Pyrite S treatment	Soil water content	pH			$S_4O_6^{=}$-S + $S_2O_3^{=}$-S		
		14[a]	28[a]	42[a]	14[a]	28[a]	42[a]
µg/g soil	%WHC[b]				µg/g soil		
		Storden s1					
0	50	7.7	7.9	7.8	0	0	0
0	100	7.6	8.0	8,0	0	0	0
50	50	7.6	7.5	8.0	0	0	0
50	100	7.6	7.7	8.1	0	0	0
100	50	7.6	7.8	7.8	0	0	0
100	100	7.6	7.7	8.1	0	0	0
150	50	7.6	7.8	7.9	0	0	0
150	100	7.7	7.8	7.9	0	0	0
		Webster 1					
0	50	6.5	6.3	6.3	0	0	0
0	100	6.6	6.4	6.3	0	0	0
50	50	6.5	6.4	6.4	0	0	0
50	100	6.7	6.5	6.5	0	0	0
100	50	6.6	6.3	6.3	0	0	0
100	100	6.6	6.5	6.5	0	0	0
150	50	6.5	6.4	6.3	0	0	0
150	100	6.6	6.6	6.5	0	0	0

pH. The pH decreases were smaller or did not change for the other soils. The results show that acidity generated by pyrite oxidation on these soils is not likely to have a large effect on soil pH.

SUMMARY AND CONCLUSIONS

The low content of As, Pb, and Se in waste pyrite as well as the absence of thiosulfate and tetrathionate in pyrite-amended soils indicates that these potentially toxic substances are not likely to affect crop production. Applications of pyrite at low rates (50 μg S/g soil-150 μg S/g soil) in the four soils or at 1000 μg S/g in Harps soil had little or no effect on soil pH after 6 weeks incubation.

PART II. DTPA-EXTRACTABLE IRON, MANGANESE, AND ZINC FROM IOWA SOILS FOLLOWING APPLICATIONS OF ELEMENTAL S OR PYRITE

INTRODUCTION

For years symptoms of Fe deficiency have been observed on many commercial soybean cultivars grown on calcareous soils in north-central Iowa and south-central Minnesota. de Mooy (1972) estimated that 1.8 million acres of potentially susceptible calcareous soils exist in the two-state region--of which approximately one-half million acres are planted to soybeans each year. Fe deficiency can severely reduce yields and frequently cause a complete crop failure in isolated calcareous areas within a field. However, noncalcareous soils that are not Fe deficient generally surround the problem areas. The boundary between chlorotic and normal green soybean plants is often abrupt within a field. Lindsay (1972) showed that the solubility of ferrous (Fe^{++}) and ferric (Fe^{+++}) ions decreases 100 fold and 1000 fold, respectively, for every unit increase in pH between 4 and 9. Under highly calcareous conditions, what little Fe that is in solution exists mostly in the Fe^{+++} state. Chaney et al. (1972) found that Fe^{+++} ions must be reduced to the Fe^{++} form before Fe^{++} can be absorbed by the roots. Fe inefficient plants have more difficulty in reducing low concentrations of Fe^{+++} to Fe^{++} at the roots (Elstrom and Howard, 1969), and the plants become chlorotic.

Recently Iowa State University has been developing methods to clean Iowa coal before it is burned. Some coal mined in Iowa contains up to 9% sulfur, most of it as pyrite. Coal preparation procedures can remove and recover large quantities of waste pyrite. Currently this waste

material is buried. The waste pyrite may be useful as a soil amendment to supply Fe to plants grown on highly calcareous, Fe deficient soils. The oxidation of pyrite yields sulfuric acid and Fe^{++} that can be immediately available to plants. Sulfuric acid also increases plant-available Fe indirectly through soil acidification. Some farmers in Iowa have applied elemental S to calcareous soils to acidify the soil and make more Fe available to plants, but with unknown results (R. D. Voss, extension agronomist, Iowa State University, personal communication).

This laboratory study was developed to compare the effectiveness of elemental S and waste pyrite applied to Fe deficient calcareous soils in increasing their extractable Fe, Mn, and Zn contents after two incubation periods. The possibility of the two sources of S causing Fe, Mn, and Zn toxicities on adjacent acid and calcareous soil was also examined. A modification of the diethylenetriaminepentaacetic acid (DTPA) soil test developed in Colorado by Lindsay and Norvell (1978) was used to identify treatments which alleviated Fe, Mn, and Zn deficiencies or promoted toxicities. In their procedure, the metals were extracted from air-dry soils, but in this study the metals were extracted from S-amended soils immediately after wet incubation and without air-drying prior to extraction.

Differences in extractable Fe contents between air-dry and moist-incubated soils have been studied by others. Gogan (1975) found that field-moist calcareous soils contained one-half to one-fourth the levels of DTPA-extractable Fe and Zn found in air-dry samples. Khan and Banwart (1979) found that wet-incubation of 20 soils for 7 days without

air-drying before extraction significantly reduced DTPA-extractable Fe, Zn, and Ca. Reduction (or fixation) of Fe by moist-incubation of soils was considered nonmicrobial since toluene additions did not affect extractable Fe levels. Fe fixation is reversible upon air-drying (Khan and Soltanpour, 1978). For this reason incubated soils were not air-dried before DTPA extraction.

MATERIALS AND METHODS

Soil

The four soils used were collected on the Agronomy Farm, an Iowa State University experiment farm eight miles west of Ames. Some of their chemical and physical properties are given in Table 1.

The calcareous Canisteo and Harps soils were selected for this study because soybeans grown on them often exhibit symptoms of iron chlorosis. The calcareous Storden soil is another problem soil for crop production because of its low organic matter content, low water holding capacity, and stoniness. Webster soils are often found adjacent to the other three, and could receive pyrite applications (or misapplications) during field operations.

Pyrite and Elemental S

Waste pyrite from coal produced at the Iowa Coal Project Demonstration Mine near Oskaloosa, Iowa, was obtained from the Iowa State University experimental coal preparation plant at Ames, Iowa. The pyrite was ground to pass through a 100-mesh screen (particle size <150 μm). The total S content of the material, 31.3%, was all in the pyrite form. The waste material also contained 34.7% total Fe and 0.3% total Zn. Complete analysis of the pyrite is given in Table 2.

Elemental sulfur (sublimed, J. T. Baker Chemical Co., Phillipsburg, Pa.) was passed through a 100-mesh screen before use in the experiment.

Reagents

Elemental S-glass beads mixture (20 mg S/g glass beads)--10.0 g of elemental S were mixed thoroughly with 490.0 g of washed glass beads (<60 mesh). Before use, the glass beads were washed twice with dilute HCl, three times with deionized water, and dried overnight at 105°C.

Elemental S-glass beads mixture (2 mg S/g glass beads)--40.0 g of the 2 mg S/g glass beads mixture were mixed thoroughly with 360.0 g of washed glass beads (<100 mesh) by means of a mortar and pestle.

Pyrite-glass beads mixture (20 mg S as FeS_2/g glass beads)--3.5 g of iron pyrite were mixed thoroughly with 468.5 g of washed (<60 mesh) glass beads.

Pyrite-glass beads mixture (2 mg S as FeS_2/g glass beads)-- 40.0 g of the 20 mg S as FeS_2 glass beads mixture were mixed thoroughly with 360.0 g of washed glass beads (<60 mesh).

DTPA-extracting solution (0.01 M DTPA, 0.02 M $CaCl_2$, and 0.2 M triethanolamine (TEA))--536.90 g of TEA (formula weight of 149.19) was transferred to an 18 liter container and then 1.8 liters of water was added. Then 70.800 g DTPA (diethylenetriamine pentaacetic acid, F. W. 393.35, J. T. Baker Chemical Co.) was added directly to the TEA solution and stirred until it dissolved. The solution was diluted to approximately 17.5 liters and sufficient HCl was added until the pH was exactly 7.30. Water was added to bring the final volume to 18 liters.

Experimental Procedure

Twenty gram samples of air-dried soil that had passed through a 2-mm sieve were weighed out into a 2-oz wide mouth glass bottle. Then a total of 5.000 g of an appropriate glass beads-S source mixture and/or glass beads only were added to the bottle. Sixteen rates of each S source included 0, 50, 100, 150, 200, 250, 300, 400, 500, 1000, 1500, 2000, 2500, 3000, 4000, and 5000 µg S/g soil. All treatments were in duplicate. Once the appropriate S source-glass bead mixture was added, it was thoroughly mixed with the soil with a thin glass rod. The soil-glass bead-S mixture was then brought to about 50% of water-holding capacity with the addition of 6 ml of deionized water. The bottles were capped with polyethylene (Glad Wrap, Union Carbide Corp.) and sealed with rubber bands in order to allow oxygen exchange and prevent loss of water. The samples were incubated for time periods of 20 and 40 days at 25°C. A smaller set of samples remained unincubated before extraction and included the following six rates of each S source: 0, 250, 500, 1000, 2500, and 5000 µg S/g soil. After incubation, the bottles were uncovered, 20 ml of water were added (1:1, soil:water ratio) to each, and the contents were mixed thoroughly. After 30 minutes, the pH was measured using a glass electrode. Fe, Mn and Zn were extracted by adding 20 ml of 0.01 M DTPA solution that was 0.02 M $CaCl_2$ and 0.2 M TEA with an adjusted pH of 7.30 (final concentration: 0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1 M TEA). The resulting mixture was shaken for two hours on an end-to-end shaker at 180 oscillations/min., centrifuged at 11,000 rpm on a Sorval superspeed

centrifuge (Ivan Sorvall Inc., Newtown, Conn.) for 5 minutes, and then filtered through a Whatman No. 42 filter paper. The content of Fe, Mn, and Zn in the filtrate was determined with a 303 Perkin-Elmer atomic absorption spectrophotometer using individual Fe, Mn, and Zn cathode lamps. The results were expressed in μg of Fe, Mn, or Zn per g of soil.

Preliminary analysis of variances were calculated for soil pH, extractable Fe, Mn, and Zn to determine significant overall treatment effects from soil type, incubation period, S source, S rates, and their interactions. Multiple regression prediction models were developed to relate extractable Fe, Mn, and Zn from all four soils to their organic C and inorganic C contents, to 15 S rates, and to two incubation periods for each S source.

RESULTS AND DISCUSSION

pH

Figures 1-4 show the decrease in soil pH by amending the four soils with two sources of S at 15 rates for 20 and 40 day incubation periods. A logarithmic scale represents the S applications because most of the rates were relatively low. The average pH's resulting from the S treatments on all four soils after both incubation periods are given in Appendix Tables A1-A8. pH's of unincubated air-dry controls for each soil are presented in Appendix Table A9. The analysis of variance (AOV) for pH in Table 4 shows that S source, S rate, soils, incubation period, all their two-way interactions, and two of their four three-way interactions were highly significant at the 1% level. The mean pH values due to S source, S rate, soil type, incubation period, soil*S source interaction, and soil*incubation period interaction are given in Table 5. The means of the other two-factor and three-factor interactions appear in Appendix Table A10. Comparisons among the pH means for the soils in Table 5 show that all are significantly different at the 1% level.

While both S sources decreased soil pH, the changes were 0.7 pH unit or less for the pyrite treatments regardless of soil type or incubation period as shown in Figures 1-4. For elemental S treatments, changes in soil pH were as much as eight times greater. The decrease in pH for each soil with increasing rates of elemental S or pyrite application after 40 days incubation can be seen in Figures 5 and 6,

Table 4. Analysis of variance of soil pH and DTPA-extractable Fe, Mn, and Zn data for the four soils[a]

Variables	d.f.	Mean squares			
		pH	Fe	Mn	Zn
Soil	3	67.35**	146,522.38**	3418.34**	1157.97**
Incubation period (IP)	1	0.51**	15,681.67**	360.15**	10.84
S source	1	35.19**	516.27	6890.82**	0.20
S rate[a]	14	2.45**	1,889.61**	873.54**	3.10
Soil*IP	3	0.59**	15,772.68**	333.47**	86.28**
Soil*S source	3	2.71**	1,893.12**	2431.40**	3.45
Soil*S rate	42	0.20**	836.87**	244.48**	1.86
IP*S source	1	0.29**	1,016.82*	375.00**	5.70
IP*S rate	14	0.12**	501.09**	38.15	1.30
S source*S rate	14	1.10**	47.42	788.60**	1.15
Soil*S source*S rate	42	0.22**	178.20	229.67**	1.59
Soil*IP*S source	3	0.15**	1,582.76**	302.88**	4.64
IP*S source*S rate	14	0.03**	97.45	39.45	1.22
Soil*IP*S rate	42	0.03	369.57**	31.85	1.15
Error	42	0.02	145.54	29.54	1.77
Total	239	--	--	--	--
C.V.		2.10	39.05	75.84	14.36

[a]Control plots not included in AOV.

*,**Significant at 5% level and 1% level, respectively.

Table 5. pH and DTPA-extractable Fe, Mn, and Zn (µg/g soil) of all soils as affected by incubation period (IP), S source, S rate, soil*IP interaction, and soil*S source interaction

Factors	No. of obsns		pH	Fe	Mn	Zn
Soil						
Canisteo l	60		7.2	10.8	4.1	10.4
Harps l	60		8.0	2.3	1.1	12.4
Storden sl	60		7.4	5.6	5.4	2.8
Webster l	60		5.5	104.8	18.2	11.6
Statistical Evaluation[a]		1	**	**	**	**
		2	**	ns	**	**
		3	**	ns	ns	**
Incubation period (IP)						
20 days	120		7.1**	22.8	5.9	9.1
40 days	120		7.0	39.0**	8.4**	9.5*
S source						
Pyrite S	120		7.4**	32.4	1.8	9.3
Elemental S	120		6.7	29.4	12.5**	9.3
Sulfur rate[b]						
50 µg S/g soil	16		7.5	19.9	1.5	9.4
100	16		7.5	20.4	1.5	8.9
150	16		7.4	21.3	1.6	9.1
200	16		7.4	21.3	1.6	8.6
250	16		7.3	22.0	1.6	8.9
300	16		7.3	22.9	1.7	8.6
400	16		7.2	23.8	1.8	9.3
500	16		7.2	24.2	2.0	9.1
1000	16		7.0	31.6	4.4	9.5
1500	16		6.9	34.6	7.4	9.2
2000	16		6.7	37.3	9.4	9.5
2500	16		6.6	42.3	15.4	9.8
3000	16		6.6	45.8	16.5	10.1
4000	16		6.5	46.6	19.3	9.1
5000	16		6.4	49.4	21.6	9.9

[a]Statistical analyses based on the following orthogonal comparisons:

1 Webster data vs data from the three calcareous soils
2 Harps data vs Canisteo and Storden data
3 Canisteo data vs Storden data.

[b]Multiple regression models were developed to relate extractable Fe and Mn to S rates.

*,**Significantly different at the 5% and 1% levels, respectively.

Table 5 (continued)

Factors	No. of obsns	pH	Fe	Mn	Zn
Soil*IP					
Canisteo*20 day	30	7.2	10.5	3.6	10.6
*40 day	30	7.2	11.1	4.5	10.2
Harps*20 day	30	8.0	2.7	1.2	13.3
*40 day	30	8.0	2.0	1.0	11.4
Storden*20 day	30	7.4	5.6	5.6	2.7
*40 day	30	7.4	5.6	5.1	2.9
Webster*20 day	30	5.7	72.4	13.4	9.7
*40 day	30	5.3	137.2	22.9	13.5
Soil*S source					
Canisteo*Pyrite	30	7.9	6.2	1.0	10.3
*Elemental S	30	6.6	15.3	7.1	10.5
Harps*Pyrite	30	8.2	3.0	1.1	12.1
*Elemental S	30	7.8	1.6	1.0	12.6
Storden*Pyrite	30	7.6	6.3	1.5	3.0
*Elemental S	30	7.2	4.9	9.2	2.6
Webster*Pyrite	30	6.0	113.9	3.6	11.8
*Elemental S	30	5.1	95.8	32.7	11.3

Figure 1. pH of Canisteo soil after incubation with elemental S or pyrite at 25°C

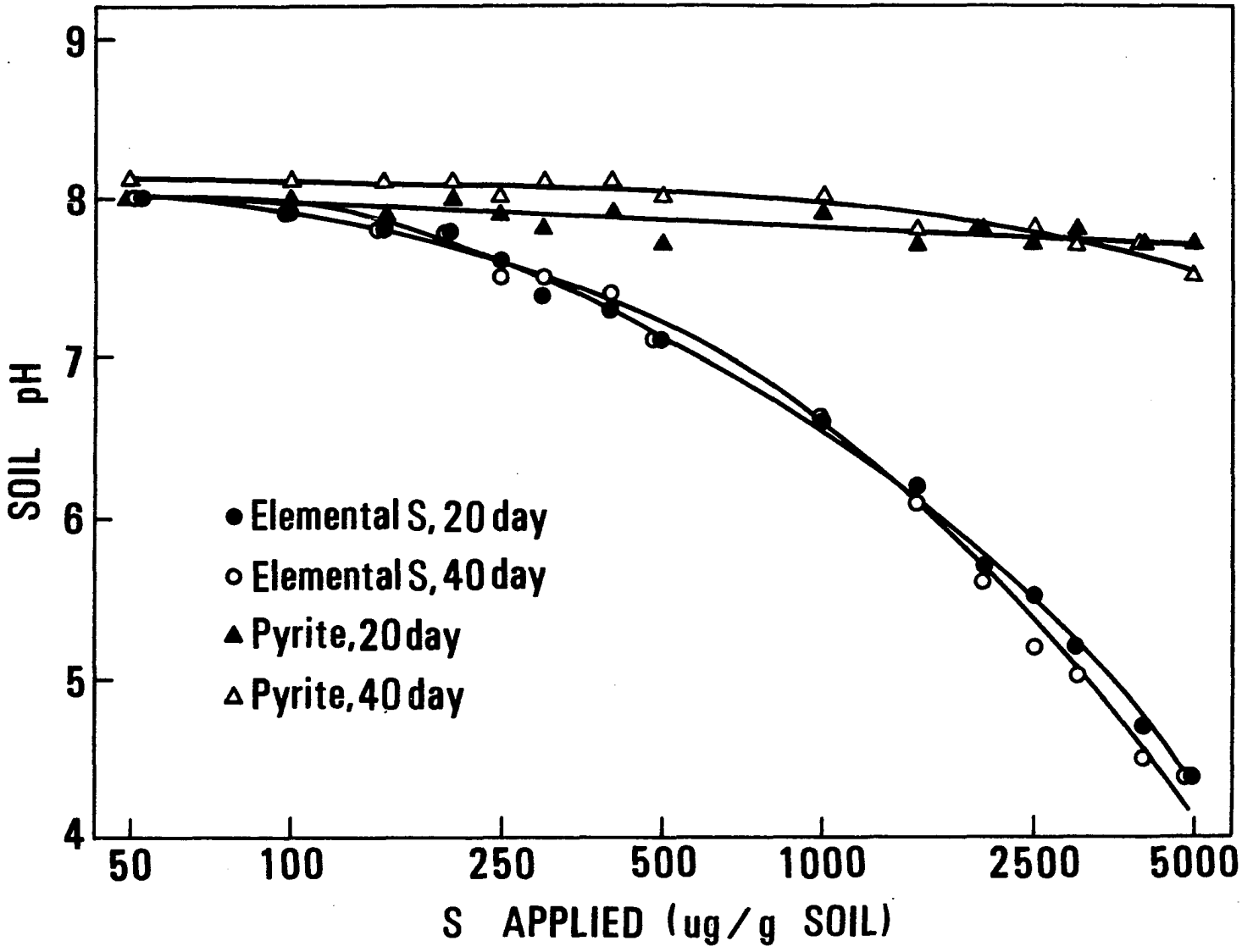

9
8
7
6
5
4
SOIL pH
● Elemental S, 20 day
○ Elemental S, 40 day
▲ Pyrite, 20 day
△ Pyrite, 40 day
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

Figure 2. pH of Harps soil after incubation with elemental S or pyrite at 25°C

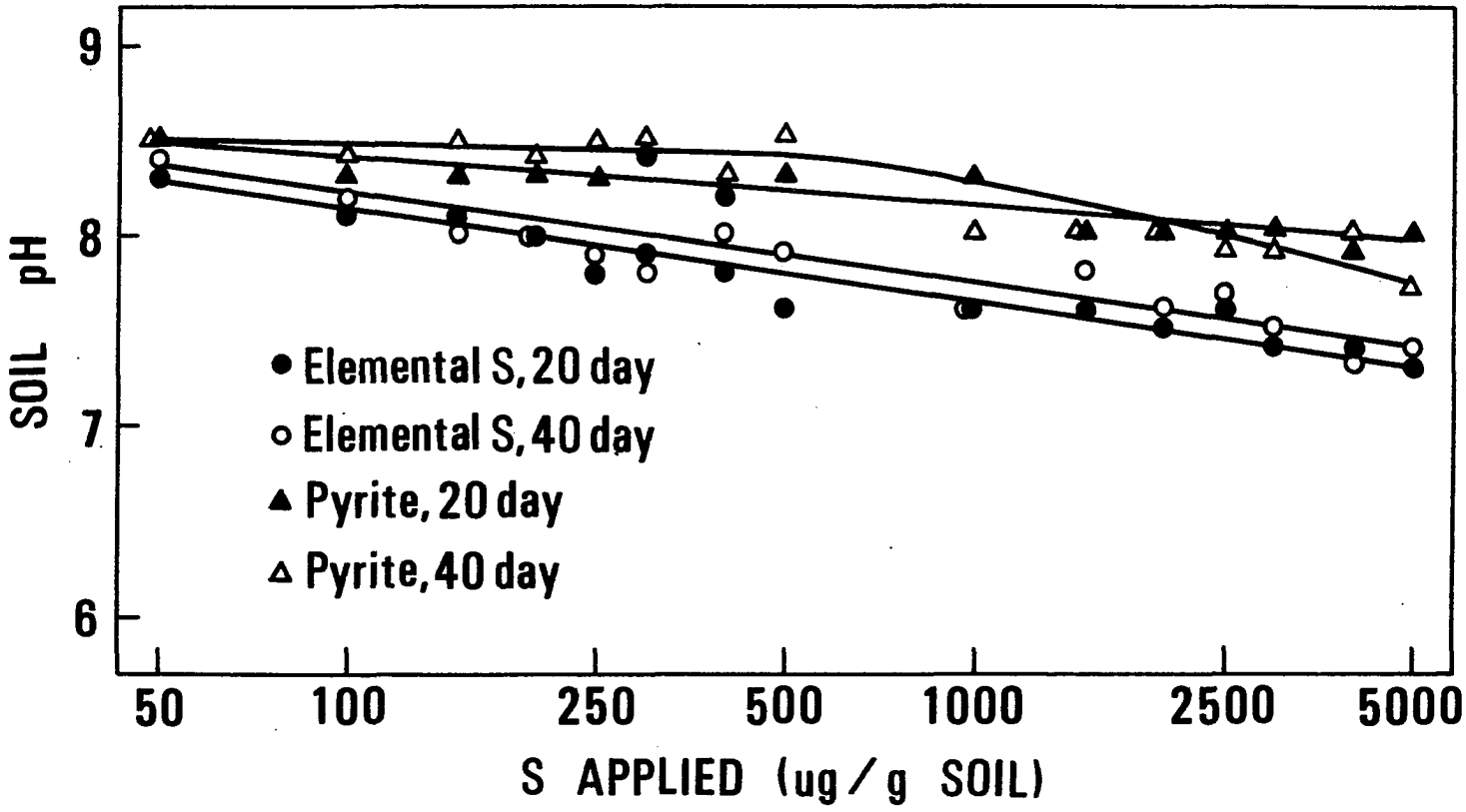

9
8
7
6
SOIL pH
● Elemental S, 20 day
○ Elemental S, 40 day
▲ Pyrite, 20 day
△ Pyrite, 40 day
50
100
250
500
1000
2500
5000
S APPLIED (ug / g SOIL)

Figure 3. pH of Storden soil after incubation with elemental S or pyrite at 25°C

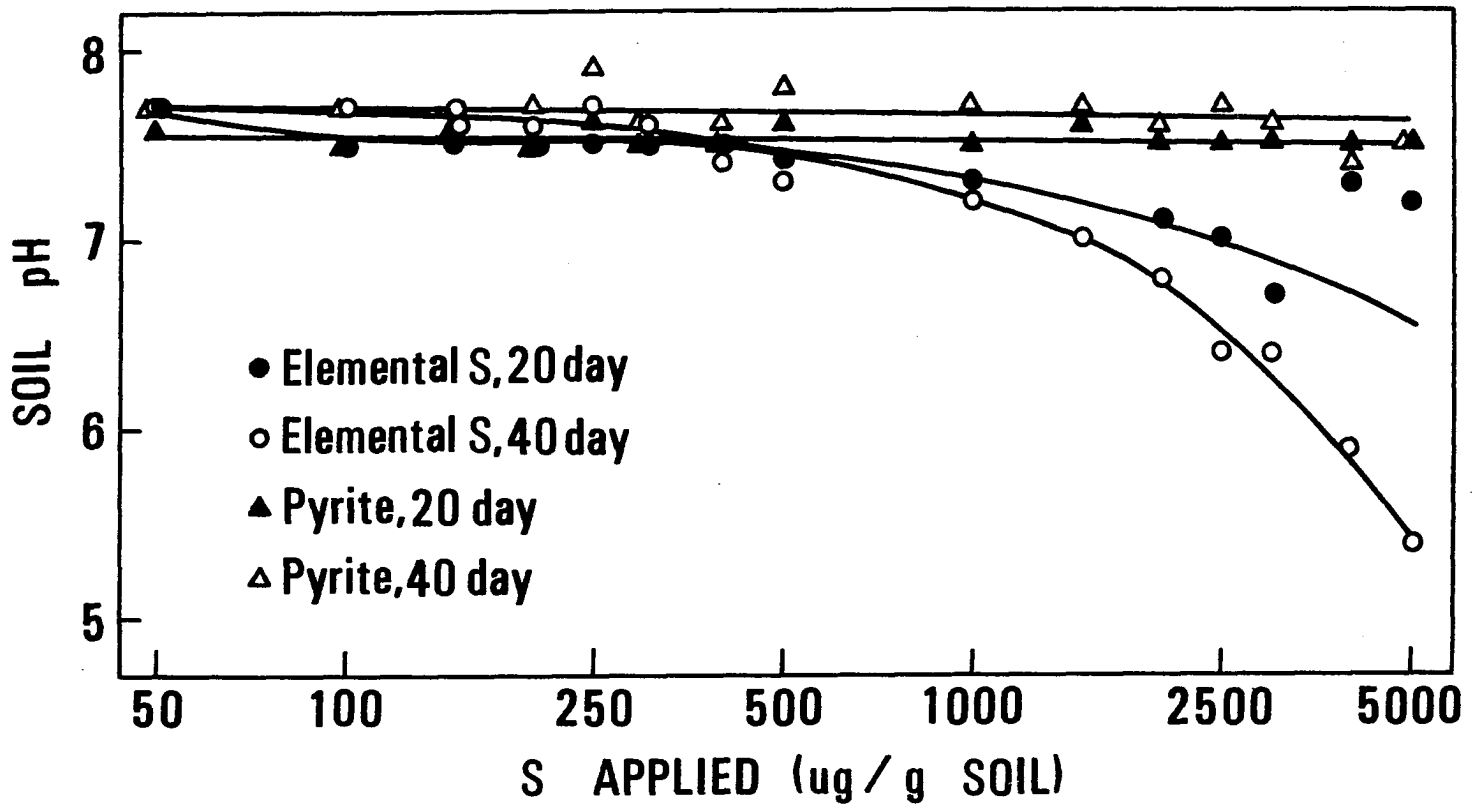

8
7
6
5
SOIL pH
● Elemental S, 20 day
○ Elemental S, 40 day
▲ Pyrite, 20 day
△ Pyrite, 40 day
50
100
250
500
1000
2500
5000
S APPLIED (ug / g SOIL)

Figure 4. pH of Webster soil after incubation with elemental S or pyrite at 25°C

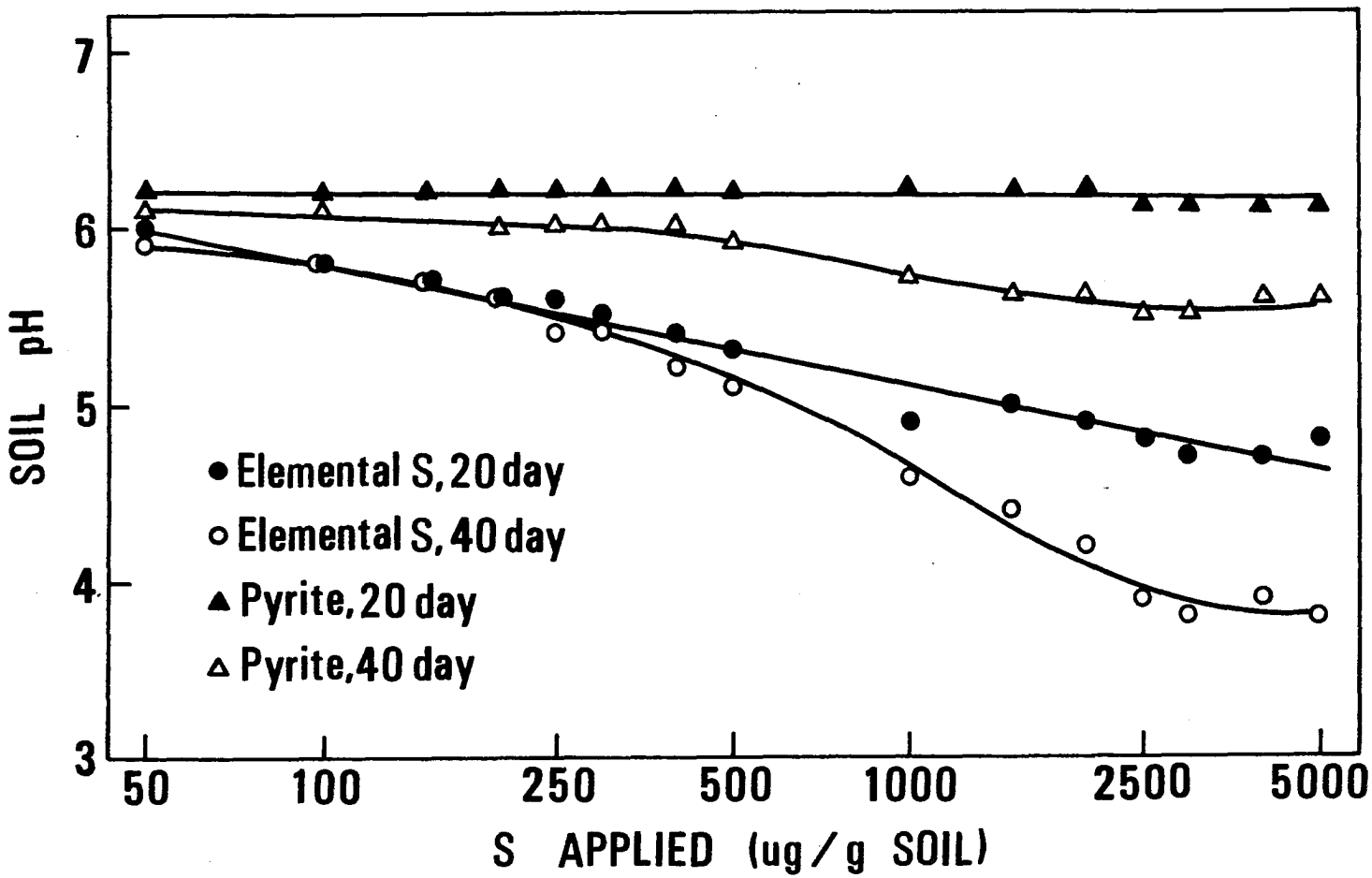

7
6
5
4
3
SOIL pH
● Elemental S, 20 day
○ Elemental S, 40 day
▲ Pyrite, 20 day
△ Pyrite, 40 day
50
100
250
500
1000
2500
5000
S APPLIED (ug / g SOIL)

Figure 5. Soil pH after 40 days incubation with elemental S at 25°C

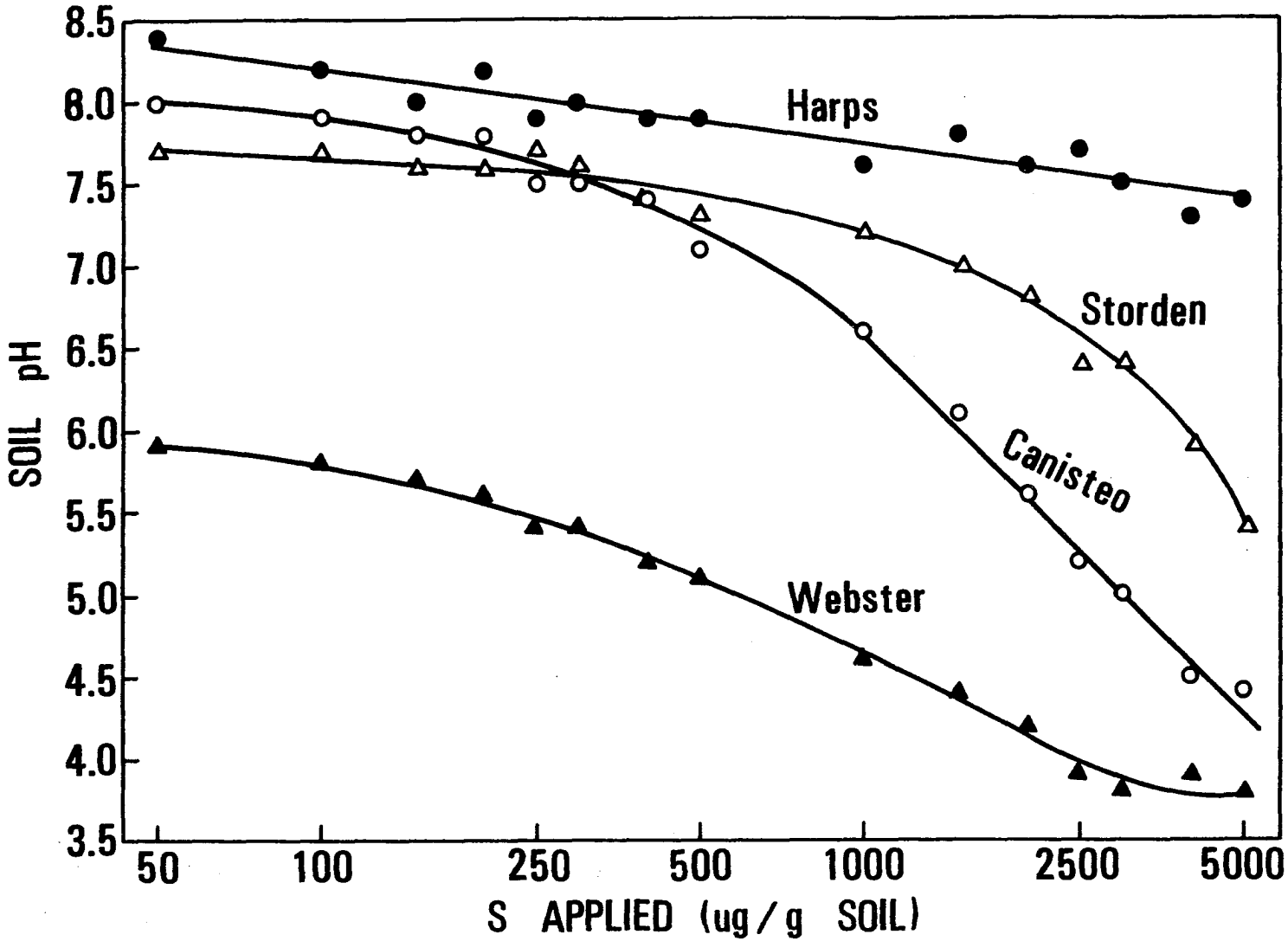
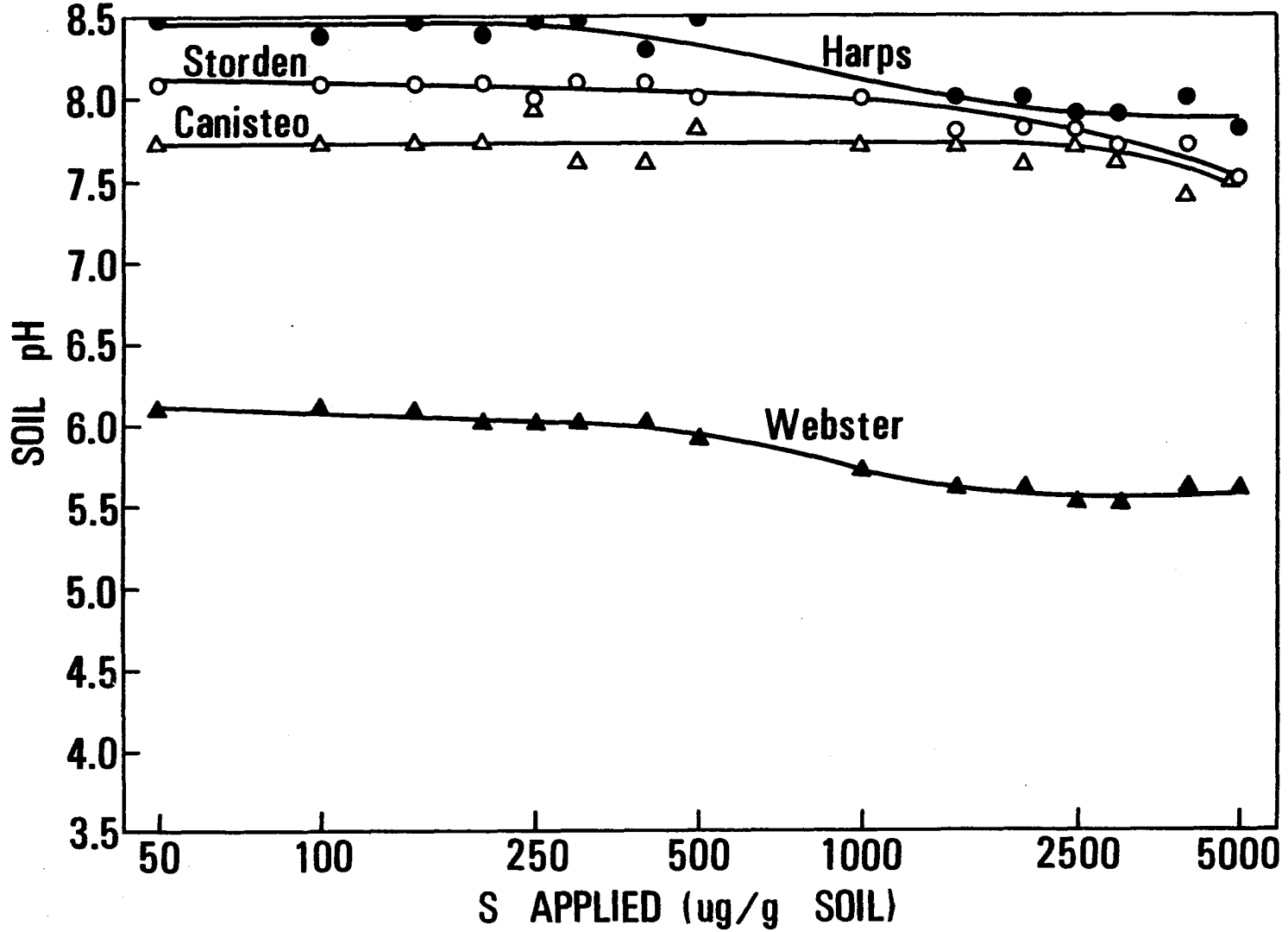

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
SOIL pH
Harps
Storden
Canisteo
Webster
50
100
250
500
1000
2500
5000
S APPLIED (ug / g SOIL)

Figure 6. Soil pH after 40 days incubation with pyrite at 25°C


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
SOIL pH
Storden
Harps
Canisteo
Webster
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

respectively. Elemental S treatments significantly lowered the pH more than pyrite, as shown in Table 5.

These results agree with the findings of others that elemental S oxidizes at much higher rates in soils than pyrite. Barrow (1971) reported that in field, glass house, and incubation experiments conducted in Australia the rate of elemental S oxidation in soils was four to five times that of pyrite of similar particle size. Oxidation of elemental S has been shown to be directly related to soil pH with higher oxidation rates on alkaline soils (Attoe and Olson, 1966; Nor and Tabatabai, 1977). Conversely, most reports show that pyrite oxidation occurs much faster at low pH's than at neutral or alkaline reaction (Quispel et al., 1952; Rassmussen, 1963; Rogoff et al., 1960); however, a few indicate that the presence of lime increases pyrite oxidation (Wiklander et al., 1950; Hart, 1959). In this study it was difficult to determine whether pyrite oxidation increased or decreased in calcareous soils solely by measuring the changes in soil pH. The decreases in soil pH were similar in the acid Webster soil and the calcareous Canisteo and Harps soils after 40 days incubation, as shown in Figure 6. The greater reactivity of elemental S coupled with the pH status of the soils would account for elemental S-incubated soils having lower pH's (higher acidity) than pyrite-amended soils for a given incubation period.

Soil pH was highly correlated to inorganic C for both pyrite ($r = 0.668$) and elemental S ($r = 0.701$) rates as shown in Table 6. Although soil pH was negatively correlated to elemental S rates at the 1% level, pyrite rates were not. Doubling the incubation period from 20

Table 6. Coefficients of correlation between DTPA-extractable Fe, Mn, Zn, and soil pH versus S rate, pH, inorganic C and organic C for each S source

Variables	S rate	pH	Inorganic C	Organic C
	Elemental S			
Fe	0.214*	-0.862**	-0.591**	0.185*
Mn	0.581**	-0.717**	-0.377**	0.027
Zn	0.051	-0.201*	0.225*	0.670**
pH	-0.471**	1.000	0.668**	-0.253**
	Pyrite			
Fe	0.195*	-0.860**	-0.485**	0.088
Mn	0.300**	-0.905	-0.517**	-0.054
Zn	0.086	-0.185*	0.159	0.635**
pH	-0.137	1.000	0.701**	0.002

*,**Significant at the 5% level and 1% level, respectively.

to 40 days reduced average soil pH slightly from 7.1 to 7.0 as shown in Table 5. Means of the soil*incubation period interaction in Table 5 show that the pH of the three calcareous soils remained virtually constant with time while the pH of the S-treated Webster soil decreased 0.4 units after 40 days. Only in Webster soil did a given S rate decrease pH more after 40 days incubation than after 20 days, regardless of S source (Figures 1-4).

For the calcareous soils, the increase in soil acidity (decrease in pH) was inversely related to the amount of carbonates present. The slightly calcareous Canisteo soil had the largest pH decrease of 3.6 units with increasing elemental S additions (Figure 1) while the highly calcareous Harps soil showed the least with a decrease of 1.1 pH units (Figure 2). At higher elemental S rates, the pH change in the moderately calcareous Storden soil and the slightly acid Webster soil was 1.8 and 1.0 pH units lower, respectively, at the end of the 40 day incubation period compared to the 20 day (Figures 3-4). Elemental S applied at high levels continued to oxidize in these soils with time, further acidifying them and lowering the pH.

A slight, nearly linear decrease in pH was noted for all pyrite-amended soils incubated for 20 days and for pyrite-amended Storden soil incubated for 40 days, as shown in Figures 1-4. A comparison of the two incubation periods for pyrite-amended Webster soil in Figure 4 shows that 0.5 of the 0.6 unit decrease occurred during the last 20 days of the 40 day incubation period. In acid soils, pyrite oxidation increases with time as measured by decreasing pH.

The decrease in soil pH (or increase in acidity) with increasing S levels demonstrates that aerobic conditions existed within the bottles which contained the incubating soils. Although Bremner and Douglas (1971) found that polyethylene film had limited permeability to oxygen and carbon dioxide, sufficient oxygen diffused through the film which sealed the incubating soils to allow S oxidation. Most microorganisms, including Thiobacillus thiooxidans, require aerobic conditions to oxidize elemental S to sulfuric acid (Starkey, 1950). The polyethylene film successfully acted as a vapor barrier in preventing water loss as all but two sealed soil samples remained moist at the end of the incubation periods.

DTPA-Extractable Fe

Effect of soil type

Figures 7-9 show the changes in DTPA-extractable Fe content after amending four soils with 15 rates of two different S sources for two incubation periods. The same data including controls for each soil and S source are given in Appendix Tables A1-A8. The Fe contents of unincubated air-dry soils at six rates for each S source are listed in Appendix Table A9. Pyrite supplied Fe in excess of the 4.5 µg Fe/g soil critical level to all three calcareous soils after 40 days incubation while elemental S supplied adequate Fe to the two least calcareous soils as shown in Figures 10 and 11.

In Colorado, the critical level of Fe necessary for adequate nutrition of corn was reported as 4.5 µg Fe/g soil from air-dry samples

Figure 7. DTPA-extractable Fe from Canisteo soil after incubation with elemental S or pyrite at 25°C

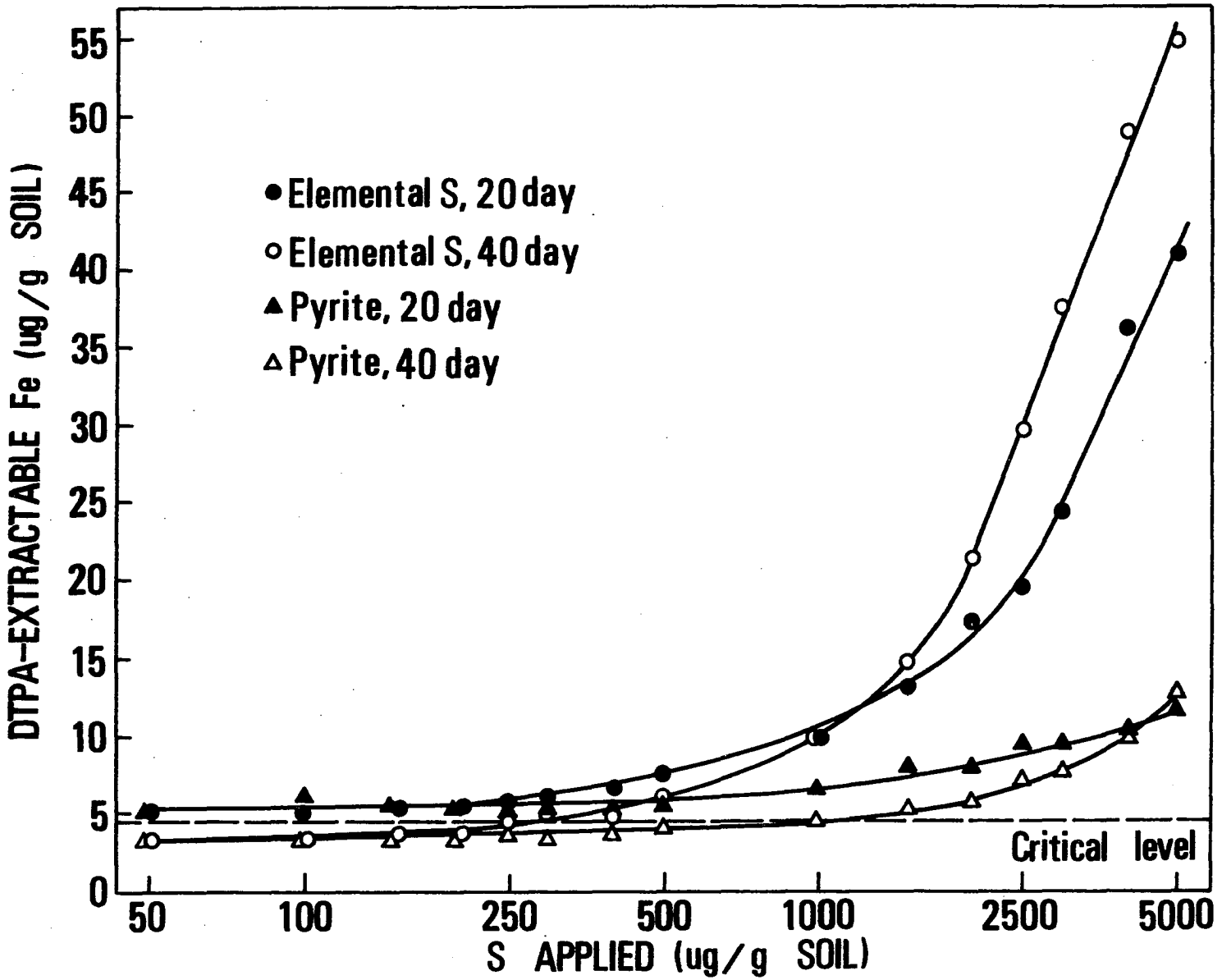

DTPA-EXTRACTABLE Fe (ug/g SOIL)
55
50
45
40
35
30
25
20
15
10
5
0
● Elemental S, 20 day
○ Elemental S, 40 day
▲ Pyrite, 20 day
△ Pyrite, 40 day
Critical level
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

Figure 8. DTPA-extractable Fe from Harps and Storden soils after incubation with elemental S or pyrite at 25°C

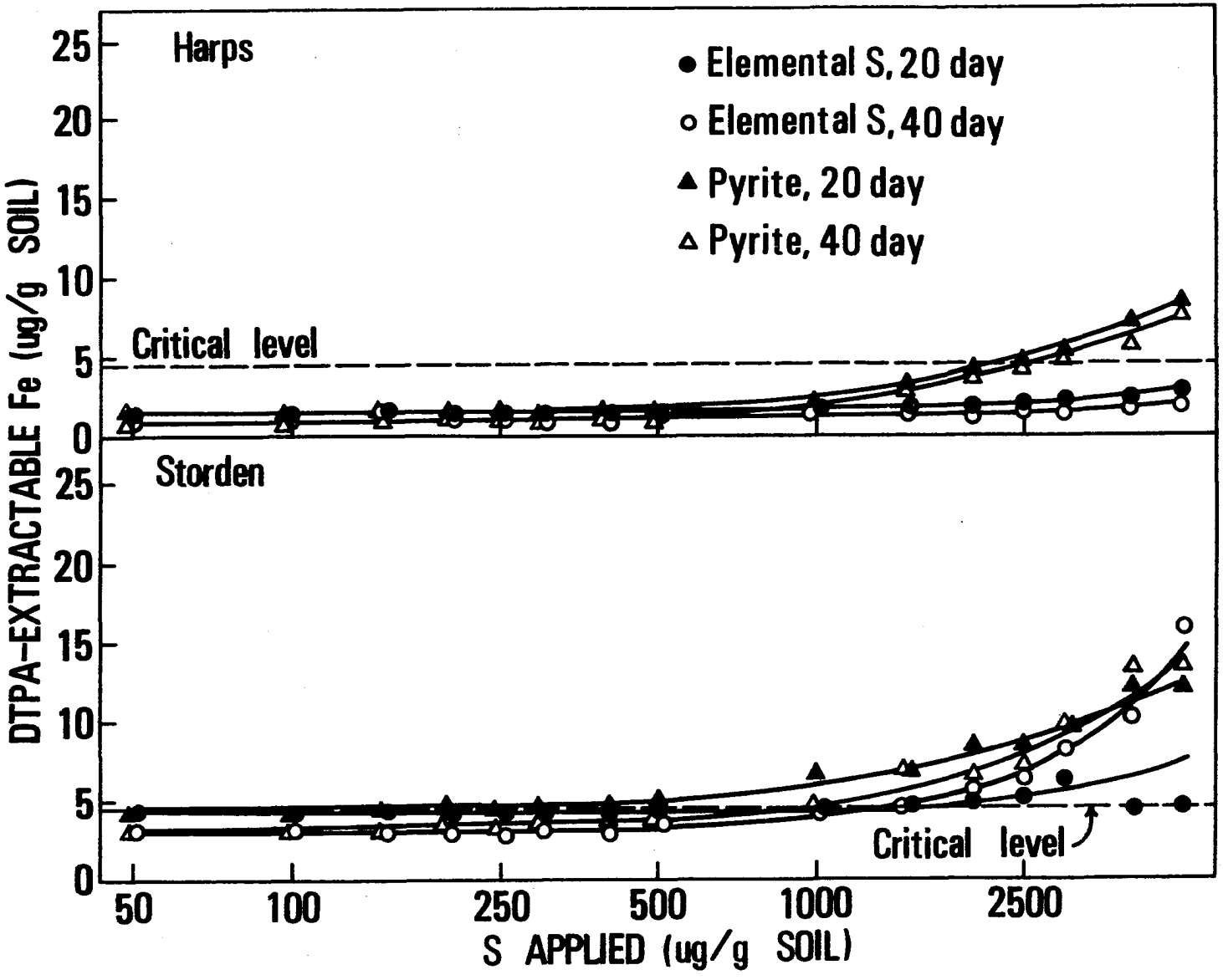

Harps
Elemental S, 20 day
Elemental S, 40 day
Pyrite, 20 day
Pyrite, 40 day
Critical level
Storden
Critical level
DTPA-EXTRACTABLE Fe (ug/g SOIL)
S APPLIED (ug/g SOIL)
0
5
10
15
20
25
50
100
250
500
1000
2500

Figure 9. DTPA-extractable Fe from Webster soil after incubation with elemental S or pyrite at 25°C

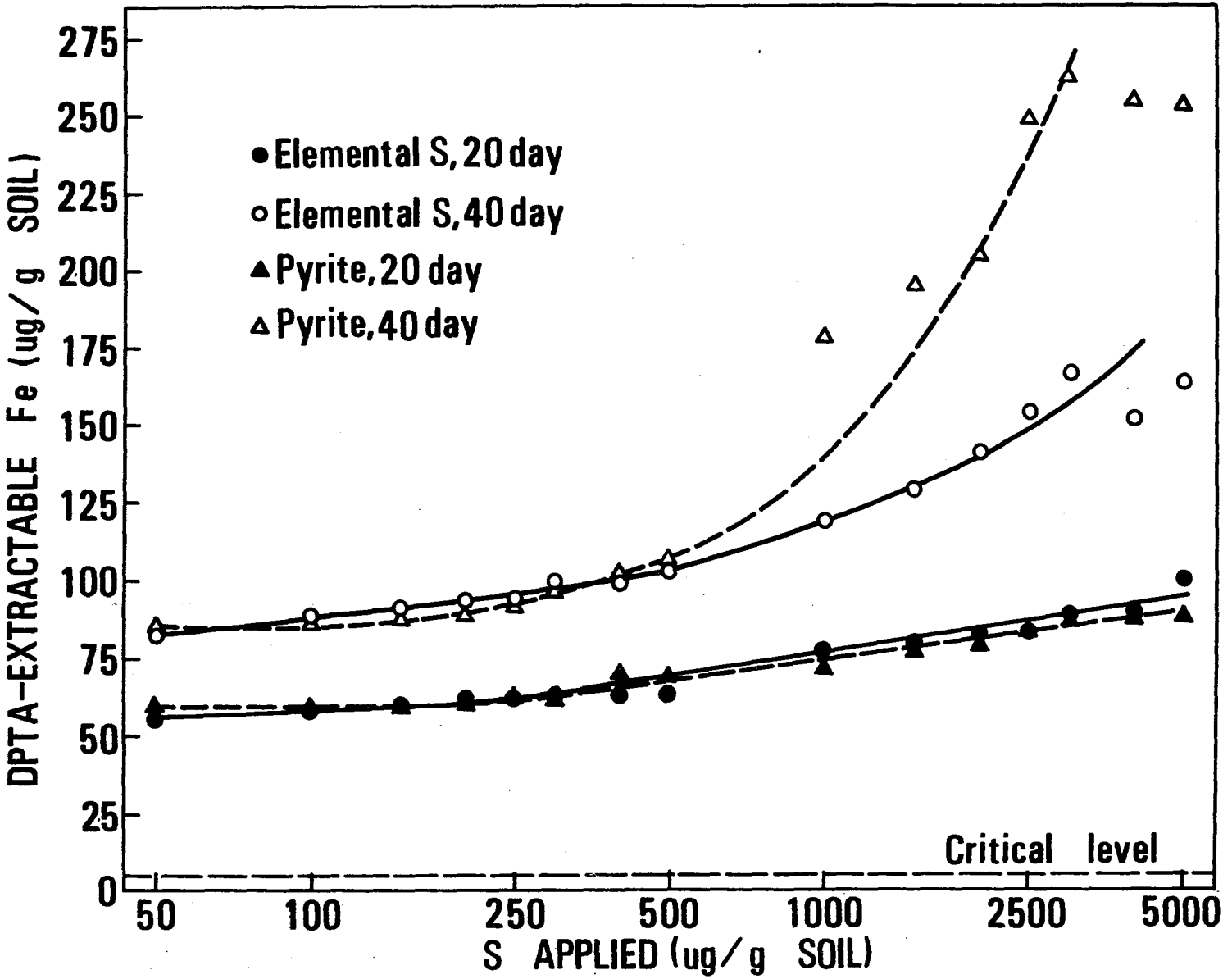

DPTA-EXTRACTABLE Fe (ug/g SOIL)
275
250
225
200
175
150
125
100
75
50
25
0
● Elemental S, 20 day
○ Elemental S, 40 day
▲ Pyrite, 20 day
△ Pyrite, 40 day
Critical level
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

Figure 10. DTPA-extractable Fe from three soils after 40 days incubation with elemental S at 25°C

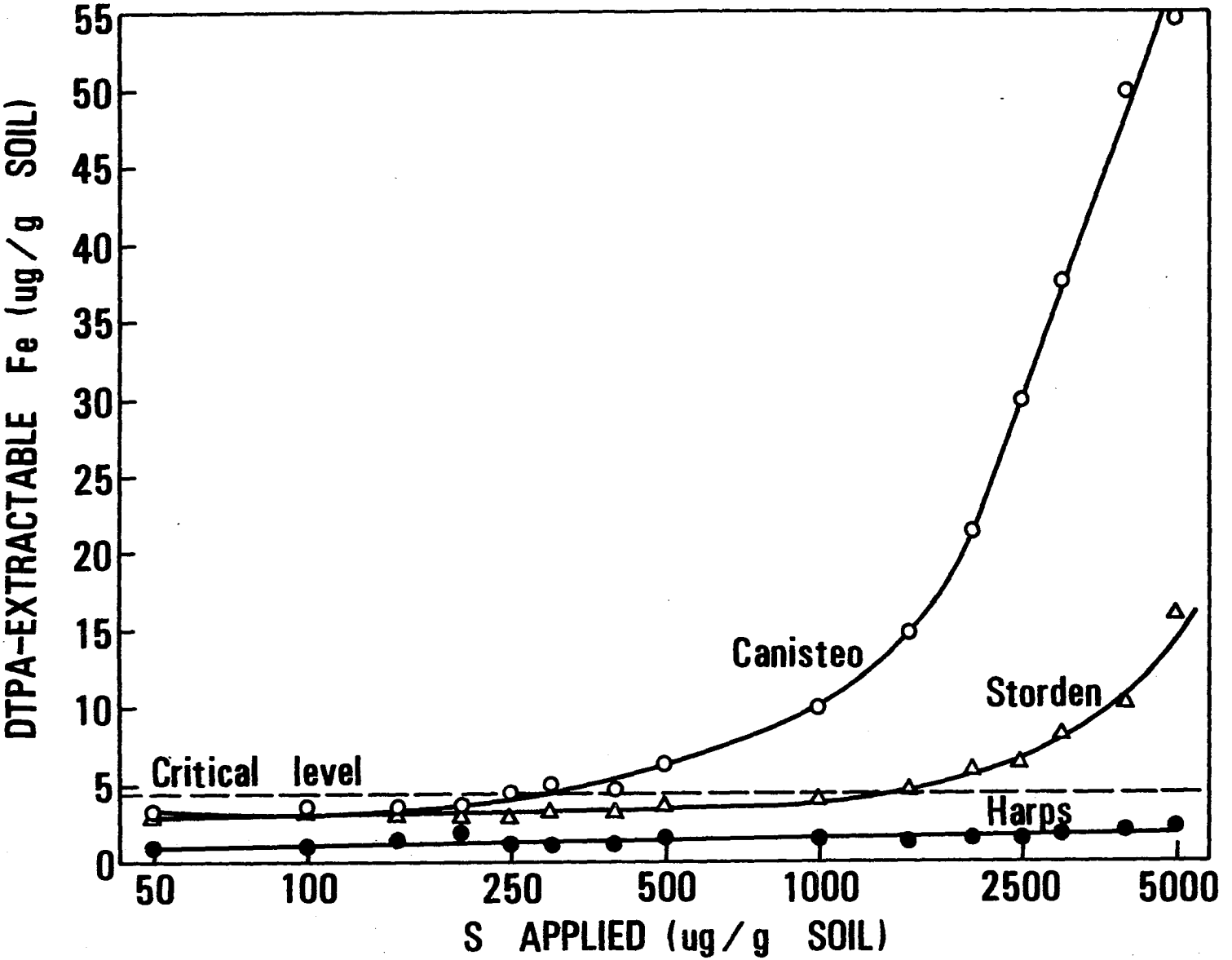

DTPA-EXTRACTABLE Fe (ug/g SOIL)
55
50
45
40
35
30
25
20
15
10
5
0
Canisteo
Storden
Critical level
Harps
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

Figure 11. DTPA-extractable Fe from three soils after 40 days incubation with pyrite at 25°C

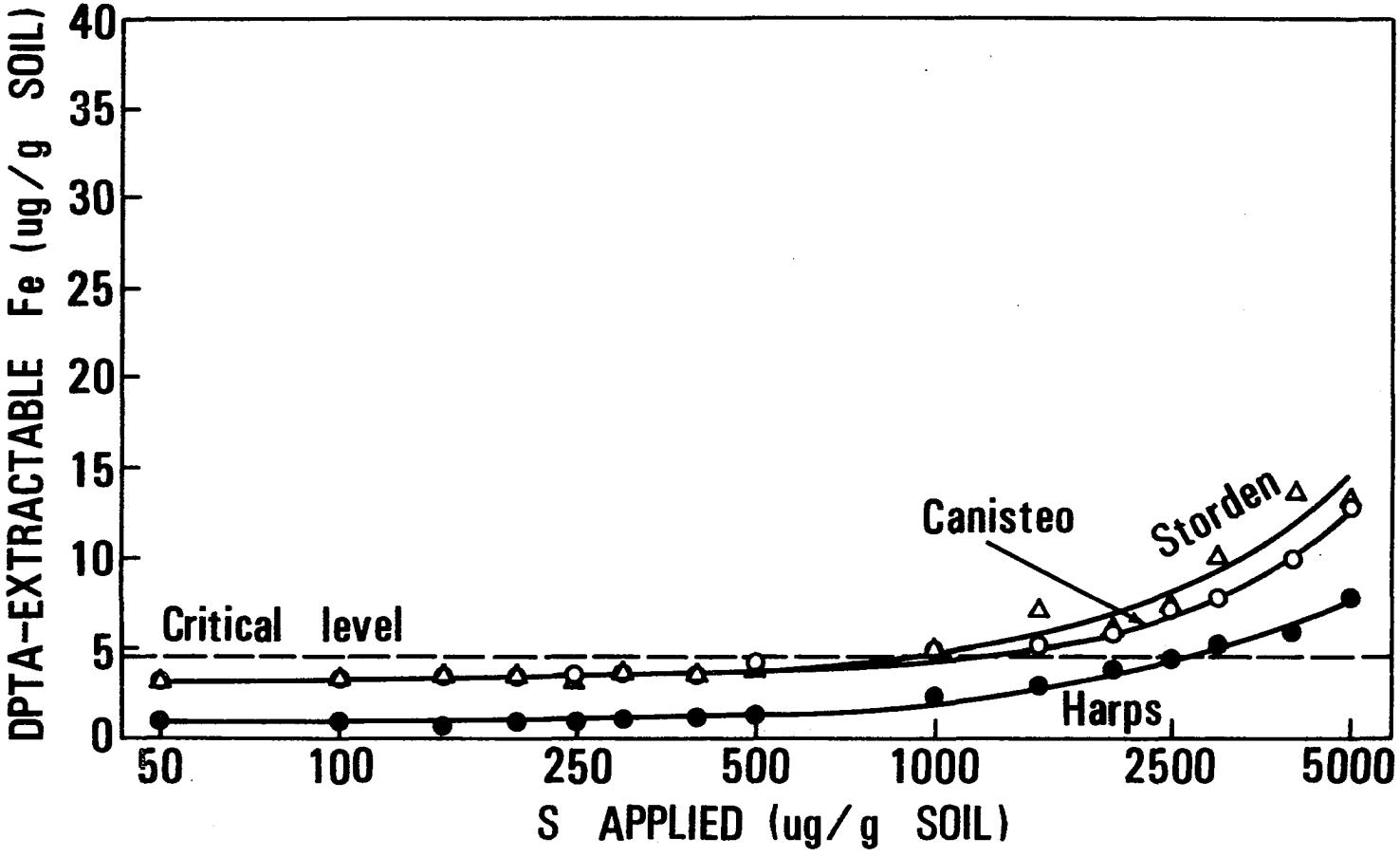
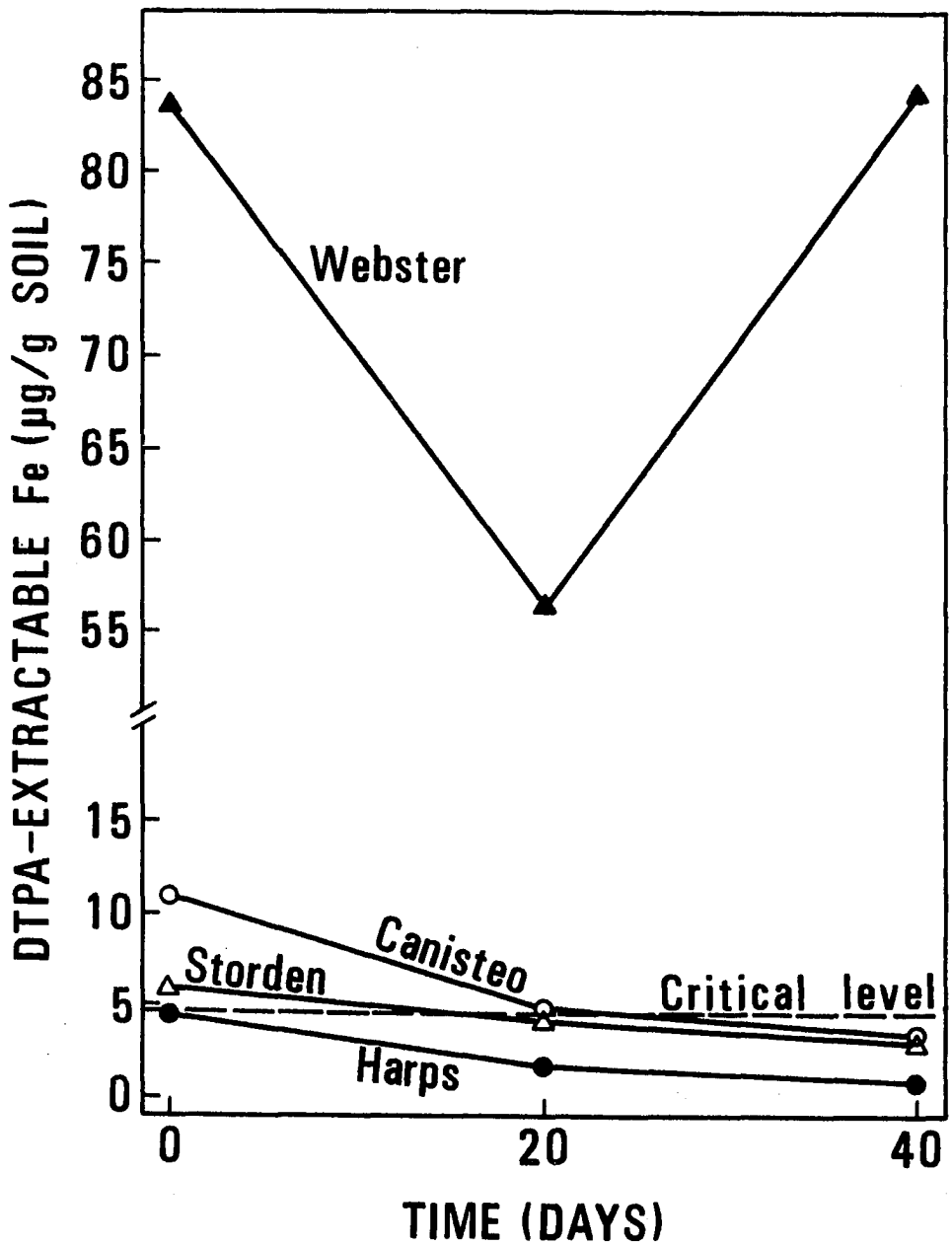

DPTA-EXTRACTABLE Fe (ug/g SOIL)
40
35
30
25
20
15
10
5
0
Critical level
Canisteo
Storden
Harps
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

Figure 12. DTPA-extractable Fe from four soils after 0, 20, and 40 days incubation at 25°C


DTPA-EXTRACTABLE Fe (µg/g SOIL)
85
80
75
70
65
60
55
15
10
5
0
Webster
Canisteo
Storden
Harps
Critical level
0
20
40
TIME (DAYS)

(Lindsay and Norvell, 1978). Because critical Fe, Mn, and Zn levels necessary for soybeans using the DTPA procedure have not been determined for Iowa soils, the critical level developed in Colorado was used. Symptoms of Fe deficiency under field conditions most frequently occur on highly calcareous Harps soil followed by the less calcareous Canisteo and Storden soils. Fe deficiency does not occur on Webster soils. Under air-dry, unincubated conditions in Figure 12, all unamended soils except Harps contained adequate Fe. The AOV in Table 4 shows that Fe is significantly affected by soil type, incubation period, and S rates at the 1% level while S source was not significant. All two-way and three-way interactions were highly significant except those containing S source*S rate terms. The mean Fe levels due to the four main effects, soil*incubation period interaction and soil*S source interaction appear in Table 5. The means of all other two-factor and all three-factor interactions appear in Appendix Table A10. Because the Fe content of Webster soil was 10 to 20 times that of the three calcareous soils, the two soils with the lowest Fe content, Harps and Storden, were not statistically different as given in Table 5. A second AOV shown in Table 7 calculated on only the calcareous soils resulted in soil type remaining significant, S source becoming significant, and incubation period becoming insignificant. The means of the four main effects, soil*incubation period interaction and soil*S source interaction appear in Table 8. The means of all other two-way and three-way interactions are given in Appendix Table A11. An analysis of the means in Table 8 reveals that the Fe content of all three soils was

Table 7. Analysis of variance of DTPA-extractable Fe and Mn data of three calcareous soils

Variables	d.f.	Mean squares	
		Fe	Mn
Soil	2	1079.72**	291.24**
Incubation period (IP)	1	0.02	0.80
S source	1	146.36**	952.20**
S rate[a]	14	201.72**	212.44**
Soil*IP	2	7.71	7.35**
Soil*S source	2	517.54**	258.50**
Soil*S rate	28	60.88**	59.21**
IP*S source	1	47.02**	3.76
IP*S rate	14	10.42**	1.69
S source*S rate	14	29.80**	191.74**
Soil*S source*S rate	28	62.91**	58.29
Soil*IP*S source	2	19.17**	4.94**
IP*S source*S rate	14	4.46	2.15*
Soil*IP*S rate	28	3.67	1.30
Error	28	2.65	0.99
Total	179	--	--
C.V.		26.13	28.37

[a]Control plots not included in AOV.

*,**Significant at the 5% level and 1% level, respectively.

Table 8. pH and DTPA-extractable Fe, Mn, and Zn (µg/g soil) of calcareous soils as affected by incubation period (IP), S source, S rate, soil*IP interaction and soil*S source interaction

Factors	No. of obsns		pH	Fe	Mn	Zn
Soil						
Canisteo 1	60		7.2	10.8	4.1	10.4
Harps 1	60		8.0	2.3	1.1	12.4
Storden sl	60		7.4	5.6	5.4	2.8
Statistical evaluation[a]		1	**	**	**	**
		2	**	**	**	**
Incubation period (IP)						
20 days	90		7.5	6.2	3.4	8.9**
40 days	90		7.5	6.2	3.6	8.2
S source						
Pyrite S	90		7.9**	5.2	1.2	8.5
Elemental S	90		7.2	7.3**	5.8**	8.6
Sulfur rates[b]						
50 µg S/g soil	12		8.0	2.9	1.0	8.2
100 "	12		7.9	3.0	1.0	7.8
150 "	12		7.9	3.3	1.0	8.5
200 "	12		7.9	3.2	1.0	7.8
250 "	12		7.9	3.3	1.0	8.2
300 "	12		7.8	3.5	1.0	7.9
400 "	12		7.7	3.7	1.0	8.3
500 "	12		7.7	4.0	1.1	8.3
1000 "	12		7.5	4.9	1.2	9.0
1500 "	12		7.4	6.2	1.7	8.6
2000 "	12		7.3	7.3	2.4	8.7
2500 "	12		7.2	8.6	7.2	9.2
3000 "	12		7.1	10.5	7.3	9.8
4000 "	12		6.9	13.6	11.7	8.5
5000 "	12		6.8	15.6	13.2	9.3

[a]Statistical analysis based on the following orthogonal comparisons:
1 Harps data vs Storden data and Canisteo data
2 Canisteo data vs Storden data.

[b]Multiple regression models were developed to relate extractable Fe and Mn to sulfur levels.

*,**Significantly different at 5% level and 1% level, respectively.

Table 8 (continued)

Factors	No. of obsns	pH	Fe	Mn	Zn
Soil*IP					
Canisteo*20 day	30	7.2	10.4	3.6	10.6
*40 day	30	7.2	11.1	4.5	10.2
Harps*20 day	30	8.0	2.7	1.2	13.2
*40 day	30	8.0	2.0	1.0	11.4
Storden*20 day	30	7.4	5.6	5.6	2.7
*40 day	30	7.4	5.6	5.2	2.9
Soil*S source					
Canisteo*Pyrite S	30	7.9	6.2	1.0	10.3
*Elemental S	30	6.6	15.3	7.1	10.5
Harps*Pyrite S	30	8.2	3.0	1.1	12.1
*Elemental S	30	7.8	1.6	1.0	12.6
Storden*Pyrite S	30	7.6	6.3	1.5	3.0
*Elemental S	30	7.2	4.9	9.3	2.6

significantly different. While the pH's of the four soils were in the order of Harps > Storden > Canisteo >>> Webster, their extractable Fe contents were in the order Webster >>> Canisteo > Storden > Harps, indicating that pH is inversely related to extractable Fe. The extractable Fe content of all four pyrite-amended soils was negatively correlated with pH ($r = -0.860$) and inorganic C ($r = -0.391$) at 1% significance but positively correlated with pyrite level ($r = 0.195$) at 5% significance in Table 6. For elemental S-amended soils, Fe was also negatively correlated with pH ($r = -0.862$) and inorganic C ($r = -0.491$) at 1% significance and positively correlated with elemental S rates ($r = 0.214$) and organic C ($r = 0.185$) at 5% significance.

Effect of S source

The effect of both S sources in calcareous soils will be examined first. Although the means of the two S sources show that elemental S yielded significantly more extractable Fe than pyrite (Table 8), each S source differentially affected the extractable Fe content in the soils which accounts for the significant soil*S source interaction in Table 7. Pyrite increased extractable Fe 1.4 μg Fe/g soil more than did elemental S in Harps and Storden soils, but elemental S increased extractable Fe 91 μg Fe/g soil more than did pyrite in Canisteo soil (Table 8). In Figure 10, less than one-third the amount of elemental S was required to increase extractable Fe above the critical level in Canisteo soil compared to Storden soil. Elemental S was not effective in supplying extractable Fe equivalent to the critical level in Harps soil. Elemental S increased

extractable Fe in the soils in the following order: Canisteo > Storden > Harps, which is the reverse of their calcium carbonate content. This result would be expected since elemental S releases extractable Fe indirectly by lowering the soil pH. Elemental S in excess of 500 µg S/g Canisteo soil and 1500 µg S/g Storden soil acidified both soils and greatly increased their extractable Fe contents as shown in Figures 5 and 10.

In Figure 11, pyrite applied at rates of 1000 µg S/g, 1000 µg S/g, and 2500 µg S/g of Canisteo, Storden, and Harps soils, respectively, increased extractable Fe above the critical level. As the rate of pyrite application increased from 50 µg S to 1000 µg S/g of calcareous soil, extractable Fe increased very slightly and linearly after 40 days incubation. The Fe content of these pyrite-amended soils increased more at treatments above 1000 µg S/g soil. At the highest rate of application, Canisteo and Storden soils yielded 40% more extractable Fe than Harps. No pyrite additions raised the Fe contents of any of the three soils more than 15 µg Fe/g soil. Oxidizing pyrite serves as a continuous, direct, and slow release source of plant available Fe^{++} (Vlek and Lindsay, 1978). Under weakly acid to alkaline conditions, Fe^{++} is further oxidized to Fe^{+++} which reacts with water to form ferric hydroxide, $Fe(OH)_3$ (Vlek et al., 1974).

The ability of pyrite to supply sufficient Fe^{++} for plants depends on the rates of pyrite oxidation and ferric hydroxide precipitation as well as the amount applied. Pulford and Duncan (1975) found that soils

derived from pyritic mine spoils contained large amounts of ferric hydroxide, an amorphous iron oxide. They showed that this compound adsorbs fertilizer phosphorus, making it unavailable for uptake by plants. It is possible that applications of large amounts of pyrite could induce a phosphorus deficiency. Levels of extractable phosphorus were not measured in this study. Therefore, the long term effects of soil-applied pyrite on P availability should be evaluated before large amounts are used to correct iron chlorosis.

In Webster soils, elemental S additions increased extractable Fe nearly 90% from 56 to 99 μg Fe/g soil while the pH decreased 1.3 units from 6.1 to 4.8 after 20 days incubation as illustrated in Figures 9 and 4. During this time period, pyrite additions had no effect on soil pH although pyrite supplied nearly as much Fe at the 5000 μg S/g soil rate. At the end of the 40 day period, elemental S additions nearly doubled extractable Fe to 163 μg Fe/g soil while the pH decreased by a whole unit to pH 3.8. During the same incubation period, pyrite additions tripled extractable Fe to 253 μg Fe/g soil while the pH dropped only one-half unit to pH 5.6. This result suggests that pyrite supplies Fe both directly through oxidation and indirectly through acidification. Murphy and Walsh (1972) suggest that little likelihood of Fe toxicity problems exist with soil-applied Fe because of rapid conversion to insoluble, unavailable compounds. They noted that some soils contain in excess of 5% Fe with no apparent toxicity problems occurring.

The four unincubated soils treated with 5000 μg S as pyrite/g soil contained 5 to 11 μg Fe/g soil more than similar unincubated controls as

given in Appendix Table A9. The four unincubated soils treated with 5000 µg S as elemental S/g soil contained 0.5 to 5.0 µg Fe/g soil more than similar unincubated controls. These results show that a given rate of pyrite contains some soluble Fe compounds. Soluble Fe compounds such as $FeSO_4$ salts are likely to be already present on the surface of the pyrite as a result of previous oxidation (Morth and Smith, 1966).

Effect of incubation period

When extractable Fe levels from all four S-amended soils were statistically analyzed, significantly higher levels were obtained after 40 days incubation compared to 20 days as shown in Table 5. But when extractable Fe from the three calcareous soils were analyzed, both incubation periods supplied nearly identical levels of Fe as given in Table 8. Figures 7 and 8 illustrate that small differences in extractable Fe occurred as a result of doubling the incubation period of a given S-amended soil. Often differences in extractable Fe corresponded to differences in soil pH, especially after elemental S additions. In Figures 7 and 8, elemental S applied at high rates to Canisteo and Storden soils increased extractable Fe more after doubling the incubation period to 40 days which corresponded to lower pH's after the longer incubation period (Figure 1). Pyrite applied at 5000 µg S/g Canisteo and Storden soils further lowered the pH upon doubling the incubation period (Figures 1 and 2) and also yielded more extractable Fe (Figures 7 and 8).

Harps soil amended with elemental S produced slightly less acidity and less extractable Fe after increasing the incubation period from 20

to 40 days as shown in Figures 2 and 8. Pyrite-amended Harps soil also contained less extractable Fe after the longer incubation period (Figure 8). Canisteo and Storden soils amended with less than 250 μg S as either S source/g soil contained less Fe after 40 days incubation compared to the 20 day period as illustrated in Figures 7 and 8. The increases in Fe due to S additions up to 250 μg S/g soil were more than offset by the decrease in Fe due to the longer incubation period as shown in Figures 7 and 8. A reduction in soil acidity with time for a given low rate of either S source may not entirely explain the decrease in Fe associated with the longer incubation period. Nonmicrobial Fe fixation under prolonged wetting may explain why extractable Fe decreased slightly with time under calcareous conditions. The greatly reduced levels of extractable Fe from S-amended Webster soil after 20 days incubation compared to 40 days incubation may also be due to Fe fixation as shown in Figure 9. This phenomenon may occur only temporarily in Webster soil as illustrated by the large increases in extractable Fe for every S-amended treatment after the incubation period doubled.

Harps, Storden, Canisteo, and Webster controls incubated for 20 days contained 59%, 55%, 27%, and 32% less extractable Fe than found in air-dry, unincubated controls as shown in Figure 12. An AOV shows that incubation period, soils, and their interaction significantly affect the Fe content of the controls as shown in Table 9. The 20 day incubation period reduced the Fe content of all four soils as shown in Table 10. Incubation reduced the Fe content of the calcareous soils below the critical level in Figure 12.

Table 9. Analysis of variance of DTPA-extractable Fe, Mn, and Zn of four unamended soils and of three unamended calcareous soils

Variables	d.f.	Mean squares		
		Fe	Mn	Zn
All four soils				
Soil	3	7303.35***	12.29***	142.20***
Incubation period (IP)	2	179.40***	63.39***	46.43***
Soil*IP	6	117.73***	21.74***	4.14
Error	12	0.25	0.05	1.43
Total	23			
C.V.		2.25	7.33	11.56
Three calcareous soils				
Soil	2	23.97***	17.55***	164.42***
Incubation period	2	32.43***	85.60***	32.80***
Soil*IP	4	4.29***	21.50***	4.95***
Error	9	0.19	0.05	0.17
Total	17			
C.V.		9.79	7.01	4.51

***Significantly different at the 0.1% level.

Figure 12 illustrates that doubling the incubation period further decreased the extractable Fe content of the controls of the calcareous soils, but greatly increased the Fe content of the Webster soil equivalent to its unincubated, air-dry value. An additional AOV of the Fe content from the calcareous controls (Table 9) revealed that wet incubation significantly reduced Fe levels with time as given in Table 10. The means of the three incubation periods revealed that the decreases in Fe with time are nearly linear (Table 10).

These results suggest that Fe fixation greatly reduced the extractable Fe contents of all soils incubated for 20 days. Longer incubation intensified Fe fixation in the calcareous soils but alleviated it in the Webster soil. No fixation occurred in the air-dry soils. Several investigators (Khan and Soltanpour, 1978; Khan and Banwart, 1979) have suggested that decreased DTPA-extractable Fe upon incubation of moist soils may partially explain the frequent occurrence of Fe chlorosis under field conditions associated with prolonged wetting (Burtch et al., 1948; Elgala and Maier; Khan and Soltanpour, 1978; Mortvedt, 1975; Mortvedt et al., 1977; and Wallace et al., 1976b).

No adequate hypothesis has been advanced to explain reduced availability of Fe upon wet incubation of soils. Chapman (1939) proposed that wetting may coat Fe minerals with carbonates and reduce Fe availability. This explanation does not account for the reduced Fe availability of acid Webster soil after 20 days incubation or the increase in Fe availability equivalent to air-dry samples after 20 more days of incubation.

Table 10. Comparison of DTPA-extractable Fe, Mn and Zn of all unamended soils and the calcareous soils as affected by incubation period

Variables	No. of obsns	Fe	Mn	Zn
		µg/g soil		
Soils				
Canisteo 1	6	6.4	4.1	11.2
Harps 1	6	2.4	4.2	13.1
Storden sl	6	4.4	1.2	3.3
Webster 1	6	74.7	2.6	13.9
Incubation period (IP)[a]				
0 day	8	26.2	6.3	13.1
20 day	8	16.9	1.4	9.4
40 day	8	22.8	1.3	8.6
Incubation period (IP)[b]				
0 day	6	7.1	7.5	11.7
20 day	6	3.6	1.0	8.6
40 day	6	2.4	0.9	7.3
Soil*IP				
Canisteo*0 day	2	10.9	11.0	14.3
*20 day	2	4.9	0.6	9.8
*40 day	2	3.4	0.6	9.5
Harps*0 day	2	4.5	10.4	16.8
*20 day	2	1.8	1.2	13.0
*40 day	2	0.9	1.2	9.6
Storden*0 day	2	6.0	1.2	4.1
*20 day	2	4.3	1.3	3.0
*40 day	2	3.0	1.1	2.7
Webster*0 day	2	83.4	2.5	17.3
*20 day	2	56.6	2.7	11.8
*40 day	2	84.0	2.6	12.6

[a]Mean values for Canisteo, Harps, Storden, and Webster soils.

[b]Mean values for Canisteo, Harps, and Storden soils.

Multiple regression of DTPA-extractable Fe on selected variables

Multiple regression prediction models were developed to relate extractable Fe from the four soils to their organic C and inorganic C levels, rates of S application from each source, and two incubation periods. Since the soil variable has the dominant effect on extractable Fe in the AOV in Table 4, the organic and inorganic C levels of the four soils were included in the regressions to determine if these two parameters would explain the differences in extractable Fe among soils. The extractable Fe was transformed to the log function because of the heterogeneous variances among soils and to prevent prediction of negative values for treatment combinations having very low extractable Fe values. The log of the extractable Fe was then regressed on the cubic functions of S rate, and linear functions of organic C, inorganic C, and incubation period and all possible two- and three-factor interactions among the four variables in the following general model for each S source:

$$\log Fe = b_0 + b_1SR + b_{11}SR^2 + b_{111}SR^3 + b_2OC + b_3IC$$
$$+ b_4IP + b_{12}SR*OC + SR*IC + b_{14}SR*IP + b_{23}OC*IC + b_{24}OC*IP$$
$$+ b_{34}IC*IP + b_{123}SR*OC*IC + b_{124}SR*OC*IP + b_{134}SR*OC*IP$$
$$+ b_{234}OC*IC*IP + e$$

Log Fe, SR, OC, IC and IP are log extractable Fe, sulfur rate, organic C, inorganic C, and incubation period respectively; the b's are the partial regression coefficients; and e is the random error component. The multiple correlation coefficient (R^2) measures the fraction of the variation in the dependent variable (extractable Fe) explained by the regression on the independent variables. It was calculated from the following

equation

$$R^2 = \frac{SSR}{Sy^2}$$

where SSR is the sum of squares due to regression and Sy^2 is the total corrected sum of squares. A modified maximum R^2 improvement selection procedure with a 10% restriction using the computerized SAS program was employed to generate simplified models from the general model (Barr et al., 1976). Only the four linear variables were included in the first model to determine its R^2. Then this procedure added a variable producing the greatest increase in R^2 to the first model to obtain the second. Then a second variable was added to the model and each of the two variables (except the linear ones) in the model was compared to each variable not in the model until the largest increase in R^2 was made. The model selected was the "best" two-variable model (in addition to the four linear variables) the procedure can find. The procedure was repeated for additional variables and models until a maximum R^2 was attained with a 16 term model for pyrite and elemental S, respectively. Several models including the 16 term model generated by this procedure for pyrite and elemental S additions are given in Tables 11 and 12, respectively.

The R^2 values of the four term linear models for pyrite and elemental S were 0.463 and 0.625 respectively. Addition of the OC*IC soil interaction term to the four-term models increased R^2 values to 0.958 and 0.943, respectively. Thus the OC*IC interaction supplied more than one-half of the total sum of squares attributable to regression for pyrite and supplied nearly one-third of the total sum of squares

attributable to regression for elemental S. The maximum R^2 attained was 0.995 and 0.989 with the 16 term pyrite model and elemental S model, respectively. Thus additions of more terms improved the R^2 values of the models only slightly as shown in Tables 11 and 12.

The simplest regression models for each S source in which all terms were significant contained three first order interactions as well as the four linear variables in Table 13. The models for the two sources differ in the relative importance of the SR*OC and SR*IC interactions. For prediction of the log of the extractable Fe due to pyrite, the SR*IC interaction is more important than the SR*OC interaction but for elemental S, the SR*OC interaction is more important. Also the sign of the SR linear term is positive for pyrite and negative for elemental S. The R^2 values of 0.971 for the pyrite model and 0.965 for the elemental S model were very high as well as numerically similar in Table 13. Both soil parameters, OC and IC, and their interaction, OC*IC, are the most important ones influencing extractable Fe. Several reasons may explain why the R^2 values for both S source models are so high. First, all the variability due to soil type, the most important factor affecting extractable Fe, is present in the models by including IC, OC, and its interactions. The selected models for both S sources show that OC, IC, and OC*IC interaction have nearly equal significance on extractable Fe as shown by their similar high t-values (Table 13). For pyrite, IC was involved in all three interactions and OC in one as shown in Table 13. For elemental S both IC and OC were involved in two interactions. Second, each of the four soils came from one location, so the IC, OC,

Table 11. Regression parameters for five multiple regression models of the log of DTPA-extractable Fe on S rate (SR), organic C (OC), inorganic C (IC), and incubation period (IP) for pyrite

Variables	Regression coefficients				
	4-term model	5-term model	6-term model	7-term model	16-term model
Intercept	1.20060	9.86055	9.90036	9.77725	5.49235
SR	0.00012***	0.00012***	0.00009***	0.00009***	-0.00001
OC	-0.01160	-2.85147***	-2.85147***	-2.85147***	-1.41580***
IC	-0.94831***	-53.37297*	-53.49091**	-53.12616***	-27.33967***
IP	-0.01399	-0.01397	-0.01399	0.02705*	1.50457***
OC*IC	--	20.21296***	20.21296***	20.21296***	10.27990***
SR*IC	--	--	0.00008***	0.00008***	0.00097**
IC*IP	--	--	--	-0.12158***	-9.13384***
SR^2	--	--	--	--	-0.00001**
SR^3	--	--	--	--	0.00001
SR*OC	--	--	--	--	0.00004
SR*IP	--	--	--	--	0.00003*
OC*IP	--	--	--	--	0.49928***
SR*OC*IC	--	--	--	--	-0.00035**
SR*OC*IP	--	--	--	--	0.00001
SR*IC*IP	--	--	--	--	0.00001
OC*IC*IP	--	--	--	--	3.47200***
R^2	0.463	0.958	0.965	0.971	0.995

*,**,***Denotes 5%, 1%, and 0.1% level of significance, respectively.

Table 12. Regression parameters for five multiple regression models of the log of DTPA-extractable Fe on S rate (SR), organic C (OC), inorganic C (IC), and incubation period (IP) for elemental S

Variables	Regression coefficients				
	4-term model	5-term model	6-term model	7-term model	16-term model
Intercept	0.89105	8.26185	8.48979	8.34404	7.77553
SR	0.00011***	0.00011***	-0.00005	-0.00005*	-0.00110***
OC	0.11380*	-2.30332***	-2.38958***	-2.38958***	-2.17320***
IC	-1.14711***	-45.76766***	-45.76766***	-45.33580***	-41.30443***
IP	-0.00217	-0.00217	-0.00217	0.04641***	0.66253***
OC*IC	--	17.20399**	17.20399***	17.20399***	15.63225***
SR*OC	--	--	0.00001***	0.00006***	0.00041**
IC*IP	--	--	--	-0.14395***	-4.20392***
SR^2	--	--	--	--	-0.00001
SR^3	--	--	--	--	0.00001
SR*IC	--	--	--	--	0.00592***
SR*IP	--	--	--	--	-0.00007***
OC*IP	--	--	--	--	-0.21822***
SR*OC*IC	--	--	--	--	-0.00227***
SR*OC*IP	--	--	--	--	-0.00001*
SR*IC*IP	--	--	--	--	-0.00003**
OC*IC*IP	--	--	--	--	1.57974***
R^2	0.625	0.943	0.957	0.965	0.989

*,**,***Denotes 5%, 1%, and 0.1% level of significance, respectively.

Table 13. Regression parameters for multiple regression of the log of DTPA-extractable Fe on S rate (SR), organic C (OC), inorganic C (IC), and incubation period (IP) for two different S sources

Variables	S source			
	Pyrite		Elemental S	
	Regression coefficients	t value	Regression coefficients	t value
Intercept	9.77725		8.34404	
SR	0.00009	10.26***	-0.00005	-2.05*
OC	-2.85147	-43.30***	-2.38960	-30.46***
IC	-53.12616	-44.41***	-45.33580	-32.28***
IP	0.02705	2.04*	0.04641	2.97**
SR*OC	--	--	0.00006	6.56**
SR*IC	0.00008	5.29***	--	--
OC*IC	20.21296	43.92***	17.20399	31.83***
IC*IP	-0.12158	-5.00***	-0.14395	-5.04***
R^2	0.971	--	0.965	--

*,**,***Denotes 5%, 1%, and 0.1% level of significance, respectively.

and IC*OC values were the same for each soil type. If each soil would have come from a number of different locations, the IC and OC values for each location would also be different, and average values for IC, OC, and IC*OC interaction would need to be calculated for each soil type. The resulting R^2 values would likely be lower due to greater variation within each soil type.

The predicted extractable Fe values generated from both S source models are compared to the observed values at each S level for Canisteo, Harps, Storden, and Webster soils in Appendix Tables A12-A15, respectively. Both models generated more accurate predicted values for the three calcareous soils, especially Harps and Storden, which contained higher levels of inorganic C, than for the acid Webster.

Mn

Effect of soil type

Figures 13-15 show that increasing elemental S levels greatly increased the DTPA-extractable Mn content of all but Harps soil after two incubation periods. The same graphs show that pyrite additions caused little, if any, increase in Mn levels on the four soils. The same data, including controls, are given in Appendix Tables A1-A8. Mn extracted from unincubated, air-dry soils amended with six rates of both S sources are tabulated in Appendix Table A9. Figures 16 and 17 compare the Mn content of all four soils amended with elemental S and pyrite, respectively, after 40 days incubation. Lindsay and Norvell (1978) estimated the critical level for DTPA-extractable Mn at 1.0 for air-dry

Figure 13. DTPA-extractable Mn from Canisteo soil after incubation with elemental S or pyrite at 25°C

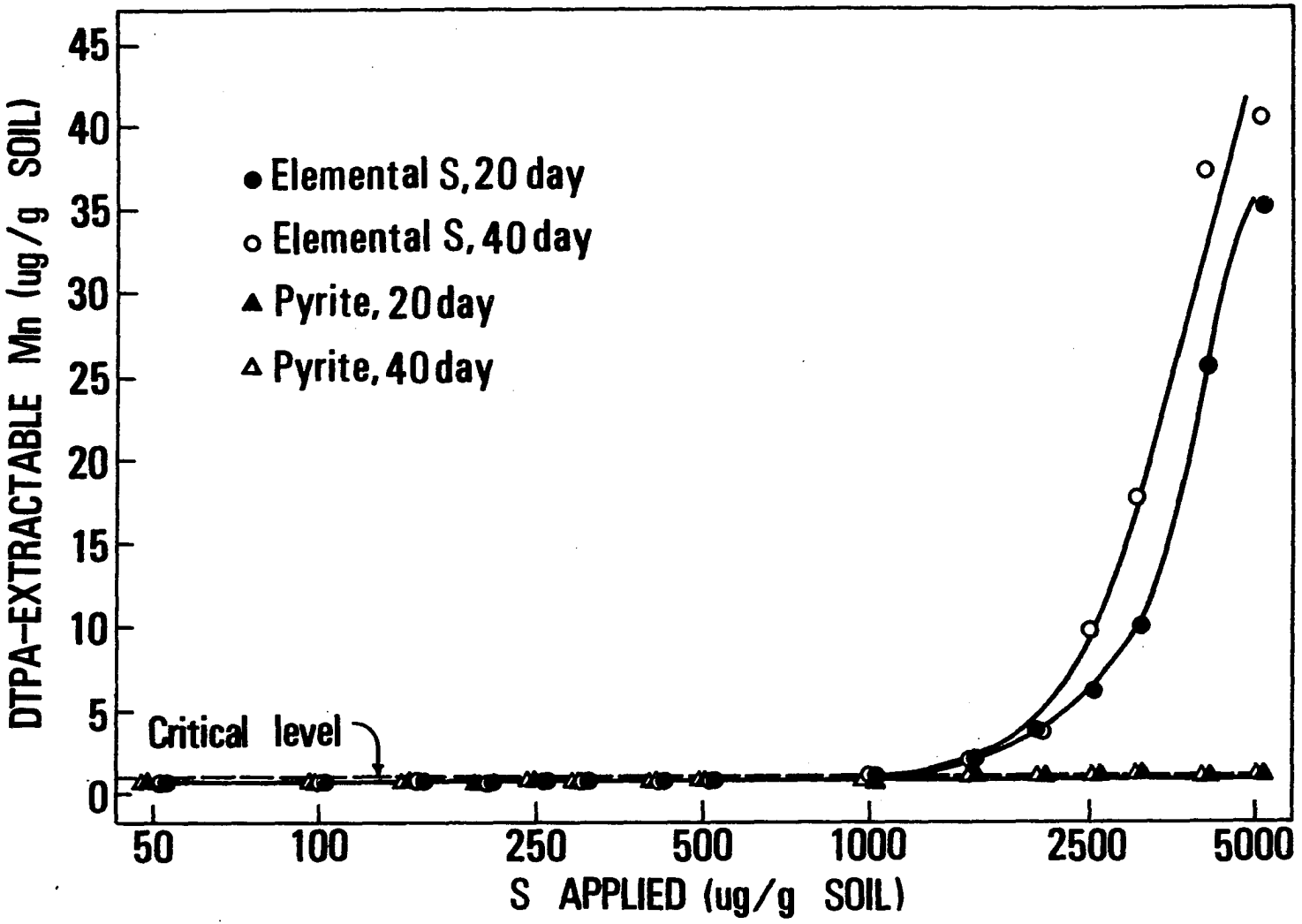

DTPA-EXTRACTABLE Mn (ug/g SOIL)
45
40
35
30
25
20
15
10
5
0
● Elemental S, 20 day
○ Elemental S, 40 day
▲ Pyrite, 20 day
△ Pyrite, 40 day
Critical level
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

Figure 14. DTPA-extractable Mn from Harps and Storden soils after incubation with elemental S or pyrite at 25°C

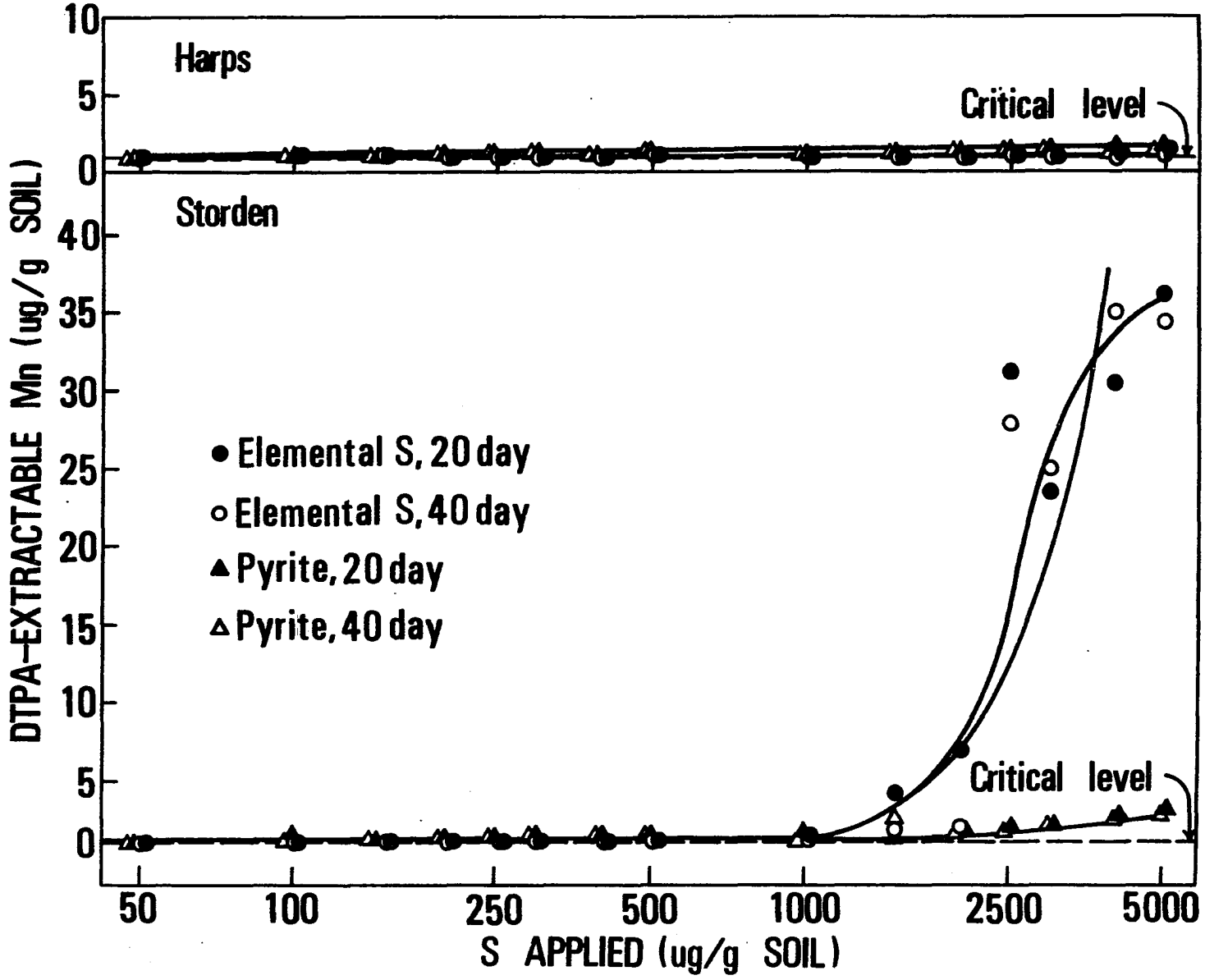

Harps
Critical level
Storden
Elemental S, 20 day
Elemental S, 40 day
Pyrite, 20 day
Pyrite, 40 day
Critical level
DTPA-EXTRACTABLE Mn (ug/g SOIL)
S APPLIED (ug/g SOIL)
10
5
0
40
35
30
25
20
15
10
5
0
50
100
250
500
1000
2500
5000

Figure 15. DTPA-extractable Mn from Webster soil after incubation with elemental S or pyrite at 25°C

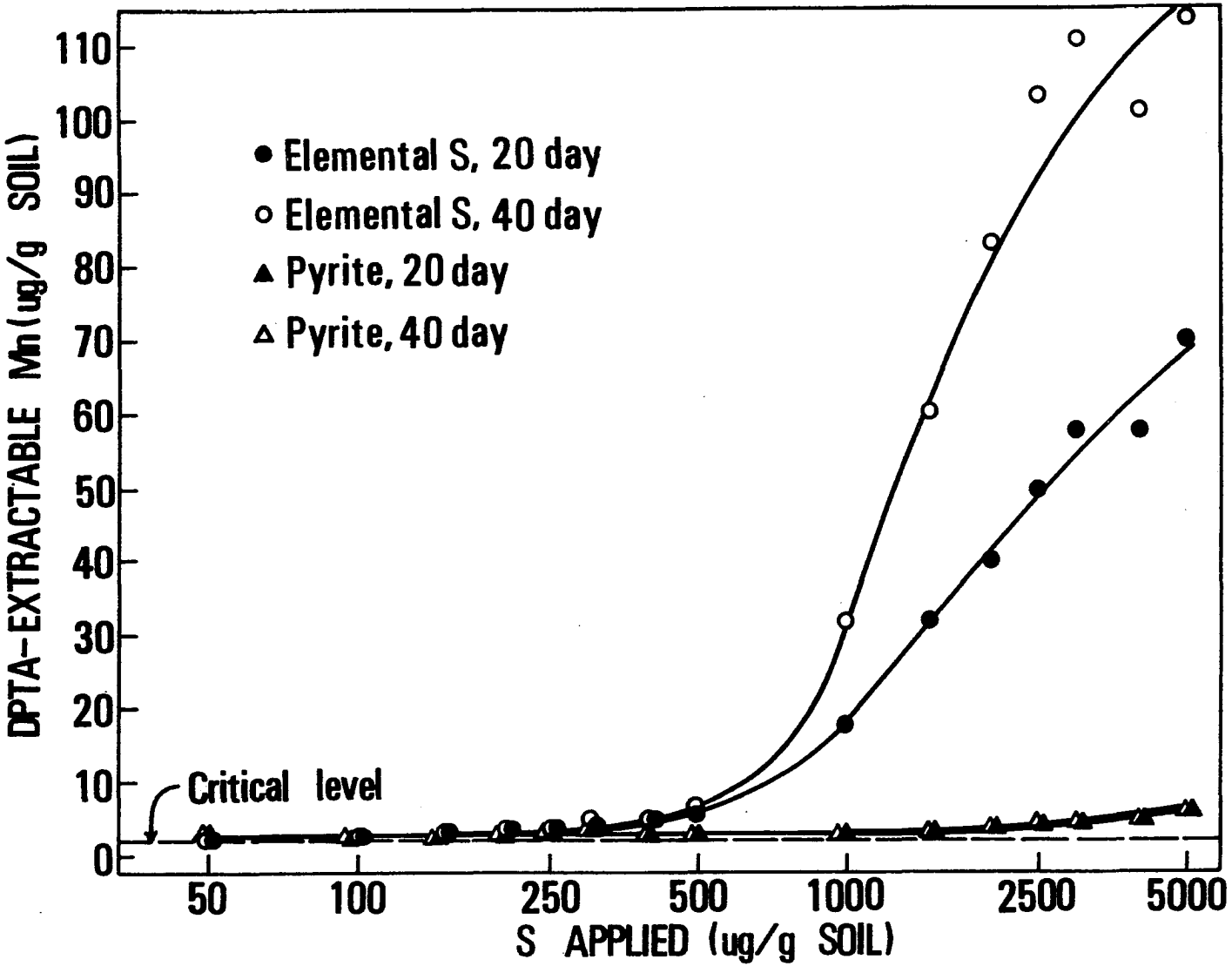

DPTA-EXTRACTABLE Mn (ug/g SOIL)
110
100
90
80
70
60
50
40
30
20
10
0
● Elemental S, 20 day
○ Elemental S, 40 day
▲ Pyrite, 20 day
△ Pyrite, 40 day
Critical level
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

Figure 16. DTPA-extractable Mn after 40 days incubation with Elemental S at 25°C

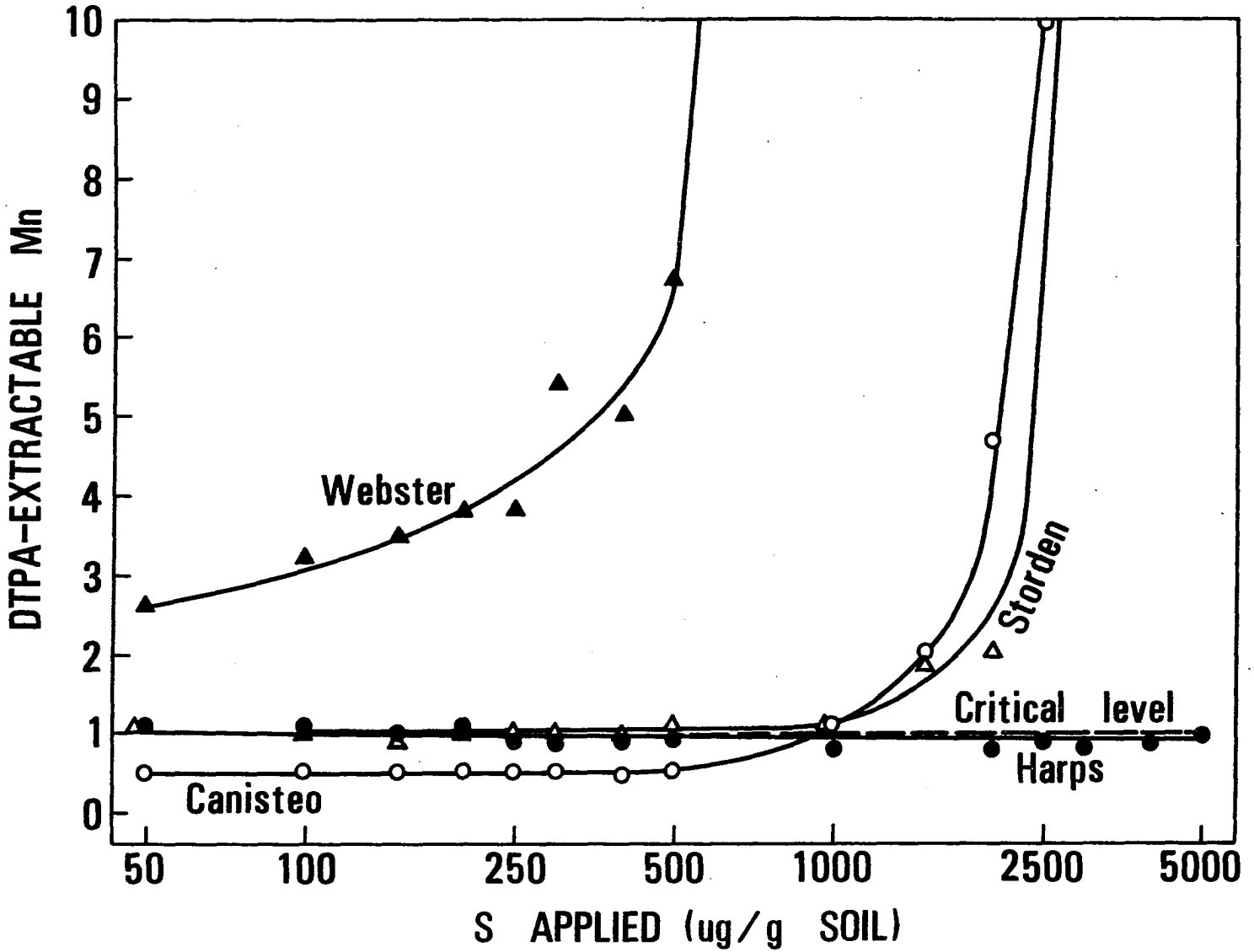
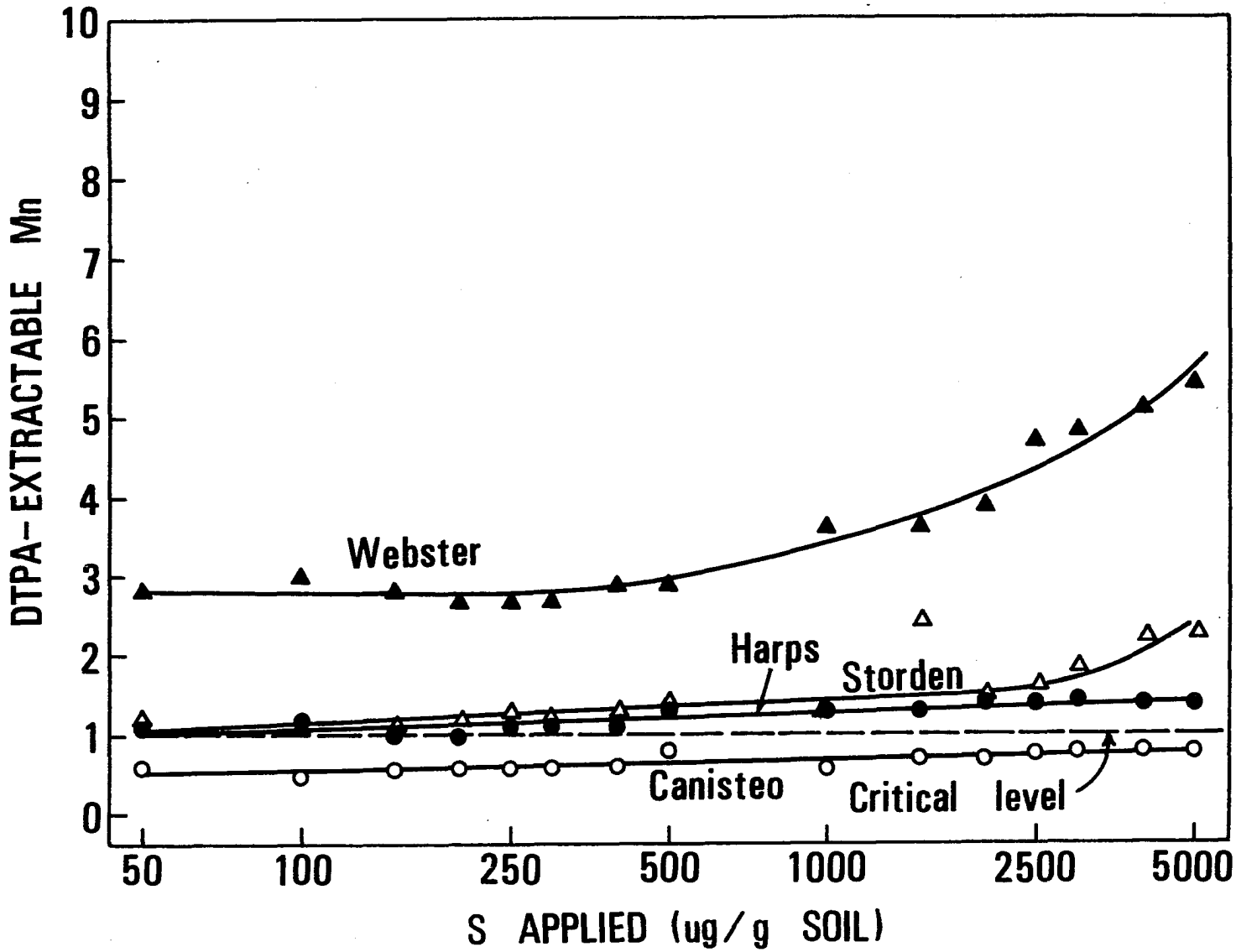

DTPA-EXTRACTABLE Mn
10
9
8
7
6
5
4
3
2
1
0
Webster
Storden
Critical level
Harps
Canisteo
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

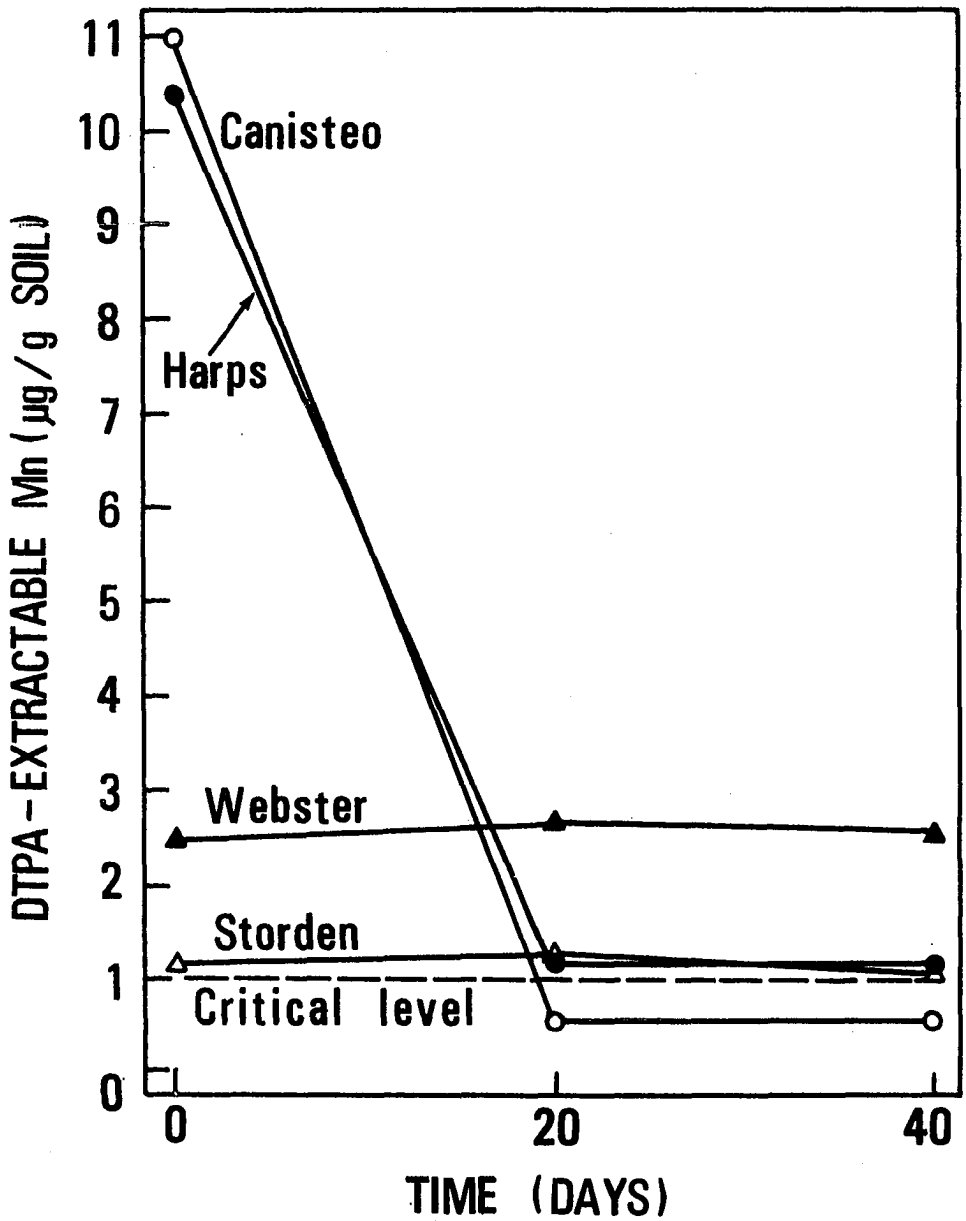
Figure 17. DTPA-extractable Mn after 40 days incubation with pyrite at 25°C


DTPA-EXTRACTABLE Mn
10
9
8
7
6
5
4
3
2
1
0
Webster
Harps
Storden
Canisteo
Critical level
50
100
250
500
1000
2500
5000
S APPLIED (ug/g SOIL)

samples. Extractable Mn levels shown in Figure 18 for all soils reveal that only unamended Canisteo soil incubated for 20 and 40 days may be deficient although unamended Harps and Storden soil contained barely adequate levels after incubation. Manganese deficiencies occur most often on well-drained soils with a neutral or alkaline pH (Murphy and Walsh, 1972) which is consistent with the low Mn content measured in the three calcareous soils in this study.

The AOV for Mn from all incubated soils in Table 4 shows that all four main effects, all but one two-factor, and all but two three-factor interactions were highly significant. The factors with the largest influence on Mn content include S source, soil type, and soil*S source interaction. Acid Webster soil contained more than three times the amount of Mn as any of the calcareous soils shown in Table 5. The mean Mn contents of these soils were in the order Webster >>> Storden > Canisteo > Harps, but Storden and Canisteo soils were not significantly different. Because of the dominating effect of Webster soil on the four-soil AOV for Mn, a second AOV was performed only on the calcareous soils as given in Table 7. All variables remained significant except incubation period and incubation period*S source interaction when compared to the four-soil AOV in Table 4. The mean Mn content of the calcareous soils was significantly different at the 1% level in the order of Storden > Canisteo > Harps. The means of the other main effects, soil*incubation period interaction and soil*S source interaction for each AOV appear in Tables 5 and 8. All other means of both AOVs are given in Appendix Tables A10 and A11.

Figure 18. DTPA-extractable Mn from four unamended soils after 0, 20, and 40 days incubation at 25°C


DTPA-EXTRACTABLE Mn (µg/g SOIL)
11
10
9
8
7
6
5
4
3
2
1
0
Canisteo
Harps
Webster
Storden
Critical level
0
20
40
TIME (DAYS)

Effect of S source

The means of the two S sources in Table 5 show that elemental S additions supplied six times the level of Mn as pyrite to the four soils. When only calcareous soils were examined, elemental S increased their Mn content nearly five times larger than pyrite as shown in Table 8. The Mn content of both pyrite-amended and elemental S-amended soils were negatively correlated with pH ($r = -0.717$, $r = -0.905$), inorganic C ($r = -0.519$, $r = -0.317$), and positively correlated to S rate ($r = 0.300$, $r = 0.581$) respectively at a 1% level of significance in Table 6. Thus decreases in pH were correlated with increases in extractable Mn.

From Figures 1-3, elemental S additions acidified all except Harps soil which corresponded to increases in Mn in Figures 13-15. Elemental S applied at 1000 µg S/g of Canisteo soil was more effective than five times this level of pyrite in yielding Mn concentrations above the critical level as shown in Figure 13. The elemental S treatment acidified the soil to pH 6.6 (Figure 1) which accounted for increased Mn availability. Acid-forming materials such as elemental S have been used to acidify soils to correct lime-induced Mn deficiency in soybeans (Garey and Barber, 1952; Tisdale and Bertramson, 1950). Applications of elemental S above 3000 µg S/g of Canisteo soil decreased the pH to 5.2 or less while the Mn content increased 10 times that of the 1000 µg S/g soil rate as shown in Figures 1 and 13. Elemental S applications above 1000 µg S/g of Storden soil also greatly increased Mn through soil acidification as shown in Figures 2 and 14. An application of elemental S at 1000 µg S/g Webster soil dropped the pH below 5.0 after 40 days

incubation and increased the Mn content to 32 µg Mn/g soil, six times greater than caused by the 500 µg S as elemental S/g soil rate as illustrated in Figures 4 and 15. At pH's between 4-5, Mn solubility may reach toxic levels (Sauchelli, 1969). Therefore, high rates of elemental S applied to acid or slightly calcareous soils may lead to severe soil acidification and Mn toxicity. Because neither S source acidified Harps soil, its Mn content increased only slightly.

Pyrite additions increased the Mn contents of Canisteo and Harps soils less than 0.5 µg Mn/g soil to 1.0 and 1.7 µg Mn/g soil, respectively, in Figures 13 and 14. Pyrite doubled the extractable Mn content to 2.8 µg Mn/g Storden soil and 5.4 µg Mn/g Webster soil, respectively, as shown in Figures 14 and 15. The small effect of pyrite on soil Mn was due to its small effect on soil acidity during the two incubation periods.

Effect of incubation period

The AOV in Table 4 for all soils shows that extractable Mn levels of the two incubation periods were significantly different. The extractable Mn levels of the two incubation periods were not significantly different in the AOV of the three calcareous soils in Table 7. In Table 5, soils incubated for 40 days contained significantly more Mn than those incubated for 20 days because Webster soil amended with elemental S contained as much as 40 µg Mn/g soil more after the longer period of incubation in Figure 15. Elemental S had more time to oxidize and to release more acidity during the 40 day period. Only small increases in

extractable Mn occurred as a result of doubling the incubation period of elemental S-amended Canisteo and Storden soils in Figures 13 and 14. Incubation period had little effect on the Mn content of any of the pyrite-amended soils or elemental S-amended Harps soil as shown in Figures 13-15.

Incubating unamended controls of Harps and Canisteo soils at 50% field moisture capacity for 20 days decreased their extractable Mn content by 90% compared to similar unincubated, air-dry controls as shown in Figure 18. Doubling the incubation period caused little change in the Mn content of these soils. Storden and Webster controls contained nearly constant levels of Mn whether the soils remained air-dry or were wet-incubated as illustrated in Figure 18. Both the AOV of the Mn content of all unamended controls and of the calcareous controls show that soil, incubation period, and their interaction are highly significant (Table 9). The significance of these variables is due to the high content of Mn in the unincubated Harps and Canisteo soils in Table 10.

Gogan (1975) found that 23 Iowa soils contained an average of 25% less extractable Mn after wet incubation than similar samples that were air-dried. Khan and Soltanpour (1978) noted that 23 of 24 calcareous soils contained significantly less extractable Mn after wet incubation than air-dry samples. Air-drying these wet incubated soils did not increase the Mn content to their original levels. Sherman and Harmer (1942) recommended that soils should be tested for Mn under field-moist conditions. The results of this experiment indicate that moist soils give more consistent results for extractable Mn. It would be expected

that calcareous soils should contain less Mn than an acid soil which, in fact, occurs with moist samples but did not occur with air-dry samples of Harps and Canisteo soil.

Multiple regression of extractable Mn on selected experimental variables

Multiple regression prediction models were developed to relate DTPA-extractable Mn from the four soils to their inorganic C and organic C contents and 16 rates of each S source for two incubation periods. The same parameters used in the regressions to determine a model for extractable Fe were used to develop these models as well. Like Fe, Mn was also transformed to the log function because of the heterogeneous variances among soils and to prevent prediction of negative values for treatment combinations having very low extractable Mn values. The following general regression model used to predict the log of the extractable Mn for each S source was similar to that used to predict the log of the extractable Fe:

$$\log M_n = b_0 + b_1SR + b_{11}SR^2 + b_{111}SR^3 + b_2OC + b_3IC + b_4IP + b_{12}SR*OC + b_{13}SR*IC + b_{14}SR*IP + b_{23}OC*IC + b_{24}OC*IP + b_{34}IC*IP + b_{123}SR*OC*IC + b_{124}SR*OC*IP + b_{134}SR*OC*IP + b_{234}OC*IC*IP + e$$

Log Mn, SR, OC, IC, and IP are log extractable Mn, sulfur rate, organic C, inorganic C, and incubation period, respectively; the b's are the partial regression coefficients, and e is the random error component. The same modified maximum R^2 improvement selection procedure as used for the log Fe models was employed to generate simplified models from the

general model. The regression models generated for pyrite and elemental S including those containing only the four linear variables are given in Tables 14 and 15. The addition of the OC*IC interaction to the linear variables was more important for the pyrite models as shown by the increase of R^2 values from $R^2 = 0.303$ to $R^2 = 0.893$ compared to the elemental S models where R^2 values increased from 0.648 to 0.795. The final models selected for each S source are given in Table 16. Besides the linear variables, the pyrite model included two first order interactions while the elemental S model included one first order interaction and one cubic function. The soil parameters OC, IC, and its OC*IC interaction are the most important ones influencing extractable Mn for the pyrite model as can be seen by similar t-values in Table 16. SR is much less important. The most important factor influencing extractable Mn for the elemental S was SR followed closely by the soil factors IC, OC*IC, OC, and SR*OC*IC in Table 16. The cubic function of SR was far less important. Since elemental S has a greater influence on soil pH than pyrite, this may explain why the soil factors are more important in the pyrite model, and SR is more important for the elemental S model. The R^2 values of 0.909 for the pyrite model and 0.931 for the elemental S model were high and similar in Table 16. These values were less than the R^2 values of 0.971 for pyrite and of 0.965 for elemental S for the Fe models in Table 13.

The predicted extractable Mn values generated for both models are compared to the observed values at each SR for Canisteo, Harps, Storden, and Webster in Appendix Tables A16-A19, respectively. As in

Table 14. Regression parameters for five multiple regression models of the log of DTPA-extractable Mn on S rate (SR), organic C (OC), inorganic C (IC) and incubation period (IP) for pyrite

Variables	Regression coefficients				
	4-term model	5-term model	6-term model	7-term model	16-term model
Intercept	0.40369	3.89050	3.76210	3.71625	3.13964
SR	0.00004***	0.00004***	0.00014***	0.00016***	0.00028***
OC	-0.05951**	-1.20295***	-1.15436***	-1.14945***	-0.96942***
IC	-0.25903***	-21.36713***	-21.36713***	-21.31845***	-17.44016***
IP	-0.01282	-0.01282	-0.01282*	-0.00734	0.12855
OC*IC	--	8.13848***	8.13848***	-0.00004***	6.61394***
SR*OC	--	--	-0.00003***	8.13848***	-0.00007***
SR*IC*IP	--	--	--	-0.00001***	-0.00004***
$(SR)^2$	--	--	--	--	-0.00001
$(SR)^3$	--	--	--	--	-0.00001
SR*IC	--	--	--	--	-0.00063
SR*IP	--	--	--	--	0.00001
OC*IP	--	--	--	--	-0.04236
IC*IP	--	--	--	--	-0.95950
SR*OC*IC	--	--	--	--	0.00028*
SR*OC*IP	--	--	--	--	-0.00001
OC*IC*IP	--	--	--	--	0.37635
R^2	0.303	0.893	0.929	0.940	0.960

*,**,***Denotes 5%, 1%, and 0.1% levels of significance, respectively.

Table 15. Regression parameters for five multiple regression models of the log of DTPA-extractable Mn on S rate (SR), organic C (OC), inorganic C (IC), and incubation period (IP) for elemental S

Variables	Regression coefficients				
	4-term model	5-term model	6-term model	7-term model	16-term model
Intercept	0.47449	5.27597	5.11938	5.05494	4.30284
SR	0.00028***	0.00028***	0.00039***	0.00051***	-0.00011
OC	-0.05003	-1.62458***	-1.62458***	-1.62458***	-1.35818***
IC	-0.76616***	-29.83285***	-29.83284***	-29.83285***	-24.48145***
IP	0.01192	0.01192	0.01192	0.01192	0.50891
OC*IC	--	11.20701***	11.39840***	11.39840**	9.32262***
SR*OC*IC	--	--	-0.00014**	-0.00014**	-0.00142**
$(SR)^3$	--	--	--	0.00001***	0.00001*
$(SR)^2$	--	--	--	--	0.00001
SR*OC	--	--	--	--	0.00014
SR*IC	--	--	--	--	0.00343**
SR*IP	--	--	--	--	-0.00001
OC*IP	--	--	--	--	-0.16577
IC*IP	--	--	--	--	-3.33489
SR*OC*IP	--	--	--	--	0.00001
SR*IC*IP	--	--	--	--	-0.00003
OC*IC*IP	--	--	--	--	1.29023
R^2	0.648	0.795	0.913	0.931	0.943

*,**,***Denotes 5%, 1%, and 0.1% levels of significance, respectively.

Table 16. Regression parameters for multiple regression of the log of DTPA-extractable Mn on S rate (SR), organic C (OC), inorganic C (IC), and incubation period (IP) for two S sources

Variables	S source			
	Pyrite		Elemental S	
	Regression coefficients	t value	Regression coefficients	t value
Intercept	3.76210		5.05494	
SR	0.00014	10.64***	0.00051	20.11***
OC	-1.15436	-29.93***	- 1.62458	-15.63***
IC	-21.36713	-31.00***	-29.83284	-15.83***
IP	-0.01282	-2.13*	0.01192	0.72 ns
OC*IC	8.13848	30.63***	11.39840	15.69***
SR*OC	-0.00003	-7.50***	--	--
$(SR)^3$	--	--	-0.00001	-5.37***
SR*OC*IC	--	--	-0.00014	-13.89***
R^2	0.929		0.931	

*,***Denotes 5% and 0.1% level of significance, respectively.

the case of the regression models for Fe, both S source models generated more accurate predicted Mn values for the calcareous soils than the Webster soil.

Zn

Effect of soil type and S source

The four unincubated, unamended soils shown in Figure 19 contain eight to twelve times more Zn than shown in the original soil test analysis in Table 1. The four soils were contaminated with Zn when they were sieved through a 6 mm galvanized screen before air-drying. The air-dry soil was then used in this study. Because of the Zn contamination, only a limited portion of the Zn data will be discussed.

DTPA-extractable Zn contents of four soils amended with 15 rates of two different S sources and incubated for 20 and 40 days are presented in Appendix Tables A1-A8. The DTPA-extractable Zn contents of the same air-dry soils amended with six rates of both S sources are listed in Appendix Table A9. The AOV for the incubated treatments shows that soils, soil*incubation period interaction, and incubation period significantly affected extractable Zn as shown in Table 4. The S amendments did not significantly affect the Zn content of the soils as they did the Fe and Mn contents in Table 5. Therefore, lowering the soil pH by elemental S additions or by adding Zn via pyrite additions, which contain 0.3% Zn, had little or no effect on available Zn.

Lindsay and Norvell (1978) found the critical level for Zn in Colorado to be 0.8 μg/g Zn. Although all soils contained many times this

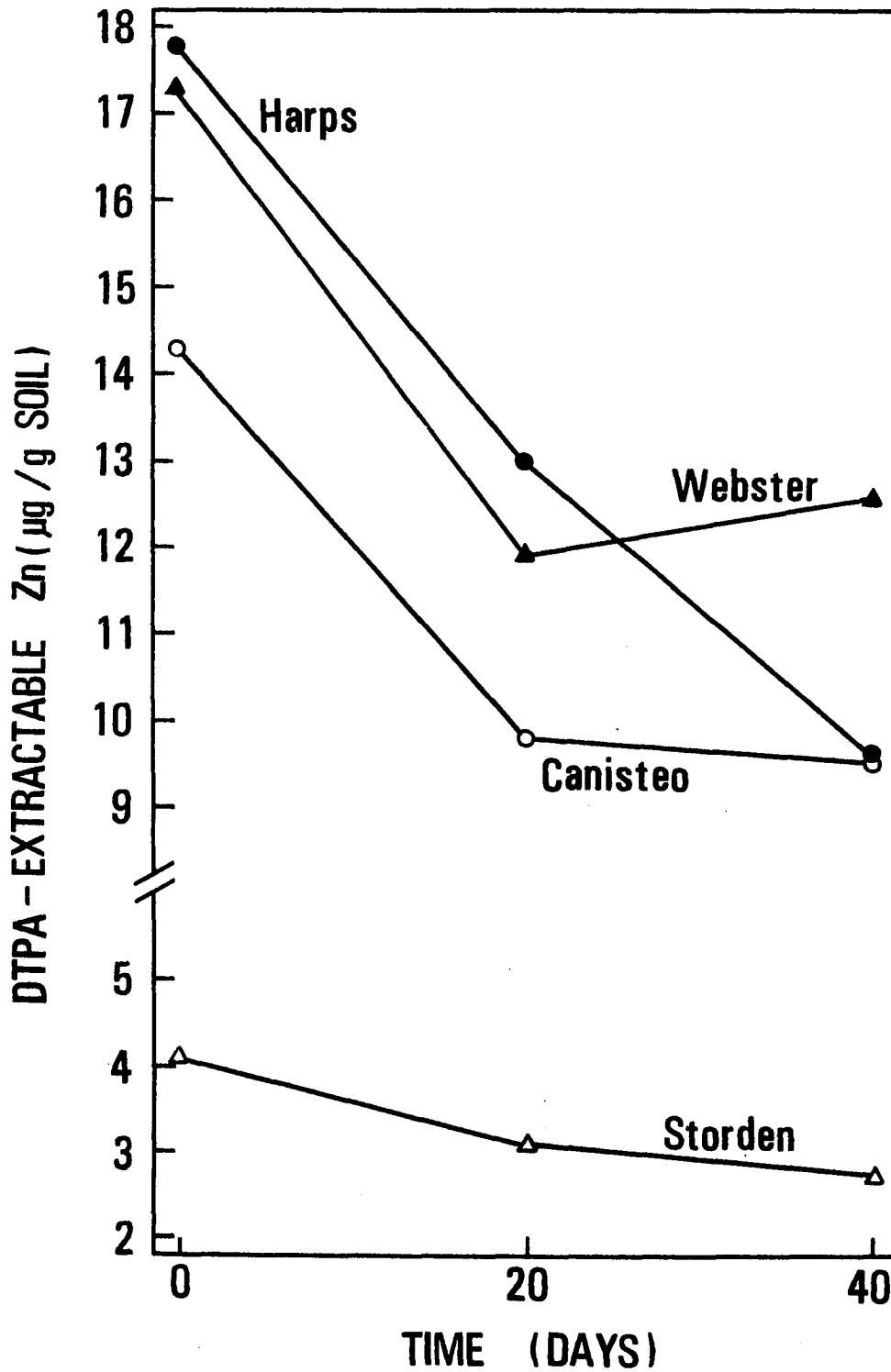
amount of Zn as seen in Figure 19, Storden exhibited less than one-third the level of Zn as found in the other three soils. Storden has one-half the organic matter content compared to the other three soils as measured by organic C content in Table 1 which may explain its relatively low Zn content. Organic matter tends to keep Zn available by forming stable complexes with it (Ellis and Knezek, 1972). Hodgson et al. (1966) found that nearly 60% of the Zn in solution is in a complexed form. Since Storden soil contains much less organic matter than the others, it would have less available Zn as well. In Table 13 extractable Zn was highly correlated to elemental S rates ($r = 0.670$) and pyrite rates ($r = 0.634$). Zn was also significantly correlated to organic C and soil pH for both S treatments. Because the S treatments were not significant, no multiple regression prediction models were developed to related added S to extractable Zn.

Effect of incubation period

The means of the soil*incubation period interaction show that doubling the incubation period from 20 to 40 days significantly decreased the Zn content of Harps soil by 1.9 µg Zn to 11.4 µg Zn and significantly increased the Zn content of Webster soil by 3.8 µg Zn to 13.5 µg Zn.

In Figure 19, the graph of the Zn contents of unamended controls with time give strong evidence that Zn fixation may have occurred on wet-incubated soils. Twenty days of wet incubation decreased the Fe and Zn contents of all soils an average of 43% and 28%, respectively, compared to air-dry soils (Figures 12 and 14). The decreases in

Figure 19. DTPA-extractable Zn from four unamended soils at 0, 20, and 40 days incubation at 25°C


18
17
16
15
14
13
12
11
10
9
5
4
3
2
0
20
40
Harps
Webster
Canisteo
Storden
DTPA-EXTRACTABLE Zn (µg/g SOIL)
TIME (DAYS)

extractable Fe and Zn were significant as shown statistically in Tables 9 and 10. Previous studies have also found that wet incubation reduced extractable Fe and Zn with Fe showing the largest reduction (Gogan, 1975; Khan and Banwart, 1979; Khan and Soltanpour, 1978). Doubling the incubation period to 40 days further decreased extractable Fe and Zn contents of calcareous soils but increased extractable Fe and Zn of the acid Webster soil. The magnitude of the increase or decrease was greater for Fe than for Zn (Figures 12 and 19). The data suggest that non-microbial Fe and Zn fixation intensifies with time under calcareous conditions. Decreased Fe and Zn availabilities that occur with prolonged wetting of calcareous soils may be partially responsible for Fe and Zn chlorosis of plants observed in the field (Burtch et al., 1948; Elgala and Maier, 1964; Khan and Soltanpour, 1978; Mortvedt, 1975; Mortvedt et al., 1977; and Wallace et al., 1976b). Under acid conditions, the Fe and Zn fixation was only temporary.

SUMMARY AND CONCLUSIONS

Although both S sources decreased soil pH, the changes in pH were 0.7 pH units or less for the pyrite treatments regardless of soil type or incubation period. The changes in pH for the elemental S treatments were as much as eight times greater. These results show that the oxidation of elemental S in soil caused greater acidity than pyrite.

As the level of either form of S increased, DTPA-extractable Fe and Mn increased while Zn remained unchanged. The regression analyses related the level of the S sources to the log of the extractable Fe and Mn content especially for calcareous soils. Pyrite treatments at 2500 µg S/g of Harps soil released quantities of Fe considered to be sufficient for plant growth whereas twice that rate of elemental S did not. Both S sources were effective in supplying Fe in the moderately calcareous Storden soil while elemental S was more effective in the slightly calcareous Canisteo soil. For the 40 day incubation period 250 µg S/g soil as elemental S supplied adequate Fe for plant growth in the Canisteo soil while 1000 µg S as pyrite/g soil was necessary to supply the same quantity of Fe. Unamended Webster soil contained adequate extractable Fe. In Webster soil, elemental S released similar amounts of Fe compared to pyrite after 20 days incubation, but pyrite released 50% more after 40 days.

Acidifying the slightly calcareous Canisteo soil with 1000 µg S as elemental S/g soil supplied Mn that was considered to be sufficient for plant growth whereas five times that rate of pyrite was needed. Elemental S added at rates of 3000 µg S/g Canisteo soil or 1000 µg S/g

Webster soil dropped the soil pH between 4.0 and 5.0 which may lead to Mn toxicity.

Although all soils contained more than adequate amounts of Zn, the Zn levels were highly correlated with the organic matter content of the soils. Storden contained one-half the organic matter and one-third the extractable Zn as compared to the other three soils. Pyrite treatments, which contained 0.3% Zn, and elemental S treatments had little effect on soil Zn levels which may be partially due to previous Zn contamination.

Fe and Zn fixation may have occurred after incubating previously air-dry soils 20 days which significantly reduced their extractable Fe and Zn contents an average of 43% and 28% in all unamended soils. Doubling the incubation period further decreased the extractable Fe and Zn levels of the three calcareous controls but increased the extractable Fe content of unamended Webster soil to its air-dry value. However, the levels of extractable Zn from the Webster controls increased only slightly after 40 days incubation. Fe fixation as measured in controls modified their extractable Fe contents and could be expected to influence extractable Fe from S-amended soils as well. Fe fixation may explain why a given rate of either S source less than 250 μg S/g Canisteo and Storden soils and a given rate of either S source applied to Harps soil supplied less extractable Fe at 40 days incubation than at 20 days incubation. Fe fixation may be temporary in S-amended Webster soil because the extractable Fe content increased greatly after 40 days incubation at all S rates when compared to the same treatments at 20

days incubation.

The length of the incubation period had little effect on the extractable Mn content of moist soils. The extractable Mn contents of air-dry Canisteo and Harps soils were many times higher than from incubated samples. These results indicate that the extractable Mn content of soils should be measured from moist, rather than air-dry, soils.

PART III. FERTILIZATION OF SOYBEANS WITH ELEMENTAL S AND PYRITE IN IOWA

INTRODUCTION

Iron deficiency can severely reduce the yield of soybeans grown in high-lime Canisteo and Harps soils of north-central Iowa and south-central Minnesota. Deficiency symptoms include an interveinal yellowing (chlorosis) of the leaves that sharply contrasts with a pattern of green veins. All leaves of severely deficient plants are affected. These plants remain stunted, shed most of their leaves at later stages of maturity, and often die. Only the young leaves may be discolored under less severe conditions. Although the plants recover during the season, their yield is reduced. Iron chlorosis may affect one-half million acres of soybeans annually in the two-state region.

De Mooy (1972) recommended applications of various iron compounds as foliar sprays for iron deficiency, but these treatments are not widely used. Soil applications of elemental S at low rates (up to 56 kg S/ha) have been used with unknown effects to correct iron chlorosis in soybeans (R. D. Voss, extension agronomist, Iowa State University, personal communication). Fuller and Lanspa (1975) reported that 100 kg S/ha applied to a calcareous soil increased the dry matter yield of two iron sensitive sorghum cultivars 15% in a glasshouse experiment. Singh (1970) found that 250 kg S/ha as elemental S prevented iron chlorosis in field-grown peas and doubled the grain yield.

Recently pyrite and pyritic materials have been examined as a source of plant available iron and sulfur (Banath and Holland, 1976; Barrau and Berg, 1977; Fuller and Lanspa, 1975). Large quantities of pyrite are recovered as a by-product of ore and coal processing

procedures. This material is considered a waste that can become a pollution hazard and presents a costly disposal problem. Iowa waste pyrite from coal processing is currently buried.

Pyrite applied to soils may have the potential to supply a constant and continuous amount of iron and sulfur for several cropping seasons. By decreasing the particle size of pyrite, workers have greatly increased its reactivity and effectiveness in supplying iron and sulfur (Banath and Holland, 1976; Vlek and Lindsay, 1978). In several glasshouse studies, pyrite or pyritic materials were applied at high rates (40-400 ton/ha) to correct Fe deficiency in susceptible sudangrass and soybean cultivars grown on highly calcareous (4-10% $CaCO_3$) soils (Barrau and Berg, 1977; Wallace et al., 1976a). No heavy metal toxicities of either crop were noted.

This experiment compared the effectiveness of elemental S applied at low rates and pyrite applied at higher rates in alleviating iron deficiency of a susceptible soybean cultivar grown in a calcareous soil in a growth chamber. Both S sources were applied at low rates to adjacent acid and calcareous soils in order to determine their effect on soybean growth.

MATERIALS AND METHODS

Soils

The four soils were collected from 0 to 15 cm of the surface at the Agronomy Farm, an Iowa State University experimental farm 8 miles west of Ames. Each soil was ground to pass a 2-mm screen, air-dried, and stored in metal storage cans until used in the growth chamber experiment. Table 1 shows some of the chemical and physical properties of the soils. Soil pH, available P, exchangeable K, soluble S, and DTPA-extractable Zn analyses were performed at the Iowa State University Soil Testing Laboratory according to the procedures described by Eik (1973, 1977). The inorganic C was determined on soil subsamples ground to <100 mesh by the method of Bundy and Bremner (1972). The particle size distribution was determined by the pipette procedure described by Kilmer and Alexander (1949).

Because these soils tested low in K, Canisteo and Harps received applications of KCl at rates of 56 and 123 kg K/ha according to Iowa State University soil test recommendations (Voss, 1968 and 1973). Harps and Webster soils tested very low and medium in P and received applications of P as $CaHPO_4 \cdot H_2O$ at rates of 101 and 34 kg P/ha, respectively. Webster soil was not amended with additional P and K.

The calcareous Canisteo and Harps soils were selected for this study because soybeans grown on them often exhibit symptoms of Fe chlorosis. The calcareous Storden soil is considered a problem soil for crop production because of its low organic matter content, its low water holding

capacity and its stoniness. Webster soils are often found adjacent to the other three, and could receive pyrite applications (or misapplications) during field operations because of its wide occurrence in the region.

Pyrite and Elemental S

Waste pyrite originating from coal mined at the Iowa Coal Project Demonstration Mine near Oskaloosa, Iowa, was collected at the Iowa State University coal preparation plant at Ames, Iowa. The pyrite was ground to pass through a 100 mesh screen (particle size <150 μm). Chemical analyses by Ames Laboratory, Iowa State University, Ames, Iowa, showed that waste pyrite contained 31.3% pyrite S, 34.7% total Fe, 0.3% total Zn, and low levels of lead, arsenic, and selenium (Table 2). Elemental sulfur (sublimed, J. T. Baker Chemical Co., Phillipsburg, Pa.) was passed through a 100 mesh screen before use in the experiment.

Description of the Growth Chamber Experiment

Two experiments were conducted. The first experiment was designed to test the effectiveness of low rates of both S sources in alleviating Fe deficiency of a susceptible commercial soybean cultivar, Wayne, grown on calcareous, Fe deficient soils. The effect of these treatments on soybeans grown on adjacent acid and calcareous soils was also studied. In a second experiment with Wayne soybeans, higher rates of pyrite were applied to the highly calcareous Harps soil. The soybean cultivar, Wayne, is very sensitive to Fe deficiency (Clark et al., 1971). The

modifying effects of soil moisture and temperature differences on soybean growth and the expression of Fe deficiency symptoms were investigated. Several reports indicate that high soil moisture levels aggravate Fe deficiency in soybeans (Elgala and Maier, 1964; Wallace et al., 1976b). Temperature extremes may cause similar effects (Wallace and Lunt, 1960).

In the first experiment, the basic application rate of elemental S was 25 μg S/g soil (56 kg/ha). Additional S treatments (50 and 75 μg S/g soil) were multiples of the base rate in order to calculate an optimum rate. A control was also included. Three pyrite treatments were applied at twice the given elemental S rates because pyrite oxidizes at rates less than one-half the rate of elemental S of similar particle size (Barrow, 1971). The elemental S and pyrite treatments were added to 1000 g of each soil and thoroughly mixed. Then each S-treated soil was placed in a 1.1 liter plastic pot having three holes in its base that allowed water drainage. The pots were placed in trays, and water was added to the soils at one of three moisture regimes: (1) high or 100% water holding capacity (WHC) twice a day, (2) moderate (medium) or 100% WHC once a day, and (3) low or 50% WHC twice a day. At high and moderate soil moisture, deionized water was added directly to the pots until the soil was saturated. Additional moisture was supplied to the soils through capillary action after flooding the trays with water. At low soil moisture, the pots were watered indirectly through capillary action by wetting a "rug" or moisture mat that covered the bottom of the trays. Flooding these trays with water saturated the rug and moistened the soil.

The pots were placed in two identical Percival growth chambers (Model No. PGW 108; Percival Manufacturing Co., Boone, Ia.), one at 25°C and the other at 30°C. Two growth chambers at different temperatures made it feasible to determine which combination of temperature, soil moisture level, and S treatment favored or inhibited Fe chlorosis.

All soils in both growth chambers were maintained at field moisture capacity for five days prior to planting five seeds per pot. At the unifoliate stage the soybeans were thinned to one plant per pot. The chlorosis index (C.I.) which measures the severity of the Fe deficiency by visual means was determined for each plant every second day after the first trifoliate leaf emerged to the end of the experiment. A C.I. of 1 indicates a normal plant, but a C.I. of 5 indicates severe chlorosis.

The plants were harvested 32 days after planting by removing the topgrowth at the soil surface. Any adhering soil was carefully removed from the stems, and the plants were placed in paper bags and dried to constant weight at 65°C. After weighing, the leaves were ground by a Wiley mill to pass through a 40 mesh stainless steel screen. The samples were stored in coin envelopes for later chemical analyses.

The second Wayne soybean experiment was similar to the first and done in the same manner except for these changes. Pyrite treatments were applied to Harps soil at the following rates: 0, 200, 400, 600, 800 and 1000 μg S/g soil). High rates of pyrite may be required to supply sufficient Fe to soybeans grown on this soil. All other factors and procedures remained the same.

Statistical Design

An unreplicated, complete factorial design was employed for both soybean experiments. In the first experiment the factors previously described included two temperatures, three soil moisture regimes, four soils, and two sources of S at four rates each. Two growth chambers, each at a different temperature, were available for use. The factor of temperature was not replicated, but the other factors were replicated in the factorial design by means of internal replication. The main effect of temperature could not be tested, but all the interactions involving temperature and the other variables were tested. The four-way interaction of temperature, soil moisture, soils, and S source served as an estimate of the experimental error.

Analysis of variances (AOV) was calculated for testing differences in (1) dry matter yield of topgrowth, (2) Chlorosis Index (C.I.), and (3) leaf nutrient composition (P, K, S, Fe, Mn, and Zn) due to the experimental treatments on soybean plants. Planned orthogonal comparisons were developed to determine the effect of increasing rates of elemental S and pyrite on plant response. In these analyses individual pyrite treatments were compared with elemental S treatments containing one-half the level of S present in the pyrite. The amount of S in the treatments was expressed as high, medium, and low according to the following:

	Qualtity S (µg S/g soil)			
S source	Control	Low	Medium	High
Elemental S	0	25	50	75
Pyrite		50	100	150

The following set of orthogonal comparisons was developed: (1) control versus S treatments, (2) elemental S versus pyrite treatments, (3) the linear effect of the treatments, (4) the quadratic effect of the treatments, (5) (the linear effect of the treatments)*(elemental S versus pyrite treatments), and (6) (the quadratic effect of the treatments)*(elemental S versus pyrite treatments) with one degree of freedom for each comparison.

A second set of planned orthogonal contrasts was developed to study the effects of soils on plant growth. The three degrees of freedom for soils was divided into the following three orthogonal contrasts: (1) Webster soil (acid) versus Canisteo, Harps and Storden soils (calcareous), (2) Storden soil (Fe sufficient) versus Harps and Canisteo soils (Fe deficient), and (3) Harps soil (severe Fe deficiency) versus Canisteo soil (moderate Fe deficiency).

The statistical analysis of the second experiment was similar to the first with the following changes. The AOV of the second experiment included two temperatures, three soil moisture regimes, and six rates of pyrite application in Harps soil.

All statistical analyses of the experimental data were performed by the IBM 360 computer at the Iowa State Computation Center using SAS procedures (Barr et al., 1976).

RESULTS AND DISCUSSION

First Growth Chamber Experiment

At least 12 plants at the low soil moisture level severely wilted and eventually died as a result of the high evapotranspiration rates within the growth chambers, especially those grown at 30°C. Because so many plants were affected, data resulting from this soil moisture level were not included in the analysis.

Soybean plants growing in Canisteo and Harps soil exhibited very mild symptoms of Fe deficiency. The characteristic interveinal yellowing appeared on the first trifoliate leaf as it developed. However, the chlorosis disappeared within two weeks, even on plants growing in Harps soil. No Fe deficiency symptoms appeared on soybeans growing in Storden and Webster soils. Because the Fe deficiency symptoms were so mild, the Chlorosis Index (C.I.) data were not analyzed.

The AOV for the dry matter yield of the topgrowth and the nutrient composition (P, K, S, Fe, Mn, and Zn) of the leaves are given in Table 17. The AOV shows differences due to soils, soil moisture regime, their interaction, but not S treatments, significantly affected dry matter yield. But by use of an orthogonal comparison on the means of the S treatments (Table 18), both S sources averaged among the three rates of application significantly increased the dry matter yield 20% more compared to the control over all soils and both soil moisture levels. The leaves of the S-treated plants contained significantly higher concentrations of S, P, and Mn compared to the controls.

Table 17. Analysis of variance of dry matter yield and leaf tissue analyses of Wayne soybean as affected by temperature, soil, soil moisture regime, and S treatment

Source	d.f.	Mean squares						
		DM[a] yield	Leaf tissue analyses					
			P	K	S	Fe	Mn	Zn
Temp	1	0.18080	0.00319	0.16355	290700.3	54.3	6.0	308.9
Error a	0	0	0	0	0	0	0	0
Soil	3	6.06682**	0.03519**	2.52494**	27149.3	5470.5**	14258.7**	1054.9*
H_2O	1	13.97316**	0.00733	0.03571	2091.6	33881.0**	1872.9**	1515.3*
S treatment	6	0.78226	0.00866**	0.04314	908949.0**	421.9	895.9**	277.8
Soil*H_2O	3	1.15639*	0.00454	0.01817	118486.4	3099.2	6057.1**	1122.3*
Soil*S treatment	18	0.30223	0.00211	0.02348	290693.9	747.5	240.4	164.4
H_2O*S treatment	6	0.04595	0.00083	0.00746	149220.5	204.5	47.4	152.1
Temp*soil	3	0.61321	0.00405	0.13058*	1490734.0**	1924.0*	182.8	633.6
Temp*H_2O	1	0.91441	0.00011	0.03223	89948.9	4325.1**	48.9	150.9
Temp*S treatment	6	0.23869	0.00221	0.01972	415433.4	538.7	205.6	522.2
Soil*H_2O*S treatment	18	0.15669	0.00199	0.02739	210679.4	709.1	105.1	226.1
Temp*soil*H_2O	3	0.09533	0.00263	0.03363	70321.0	127.1	116.1	288.4
Temp*soil*S treatment	18	0.31718	0.00249	0.03993	265370.3	615.6	178.1	446.3
Temp*H_2O*S treatment	6	0.52280	0.00043	0.01463	348269.8	391.9	84.9	162.4
Error b	18[b]	0.34872	0.00221	0.03676	158783.7	533.2	156.7	270.1
Total	111							
C.V.%		21.1	12.3	10.7	19.9	18.5	17.2	37.8

[a]DM, dry matter.

[b]16 d.f. for P, K, S, Fe, Mn and Zn due to missing plots.

*,**Significant at the 5% and 1% level of probability.

Table 18. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by S source

S[b] source	S rates	DM[a] yield/ S source	Leaf tissue concentration/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
C	0	2.4	0.31	1.62	0.13	108	56	38
ES	25, 50, 75	2.9**	0.37**	1.71	0.20**	119	74**	37
PS	50, 100, 150	2.8**	0.36**	1.71	0.19**	119	67**	38

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

**Significantly different from the control at the 1% level.

Critical nutrient levels have not been defined for plants at this stage of growth. However, according to the critical nutrient ranges developed by Jones (1966, 1968) on more mature plants, it appears that the leaves contained sufficient concentrations of all nutrients except S. The concentration of S in the leaves of the controls is below the critical level of 0.16% S required for more mature plants as reported by Kamprath et al. (1957). Besides increasing the dry matter yields, the S amendments increased the S content of the leaves by 50% compared to the controls.

These results suggest that the S treatments may have increased dry matter yields as a result of correcting an S, rather than an Fe deficiency. Visual symptoms that appeared on the leaves also give additional evidence of the presence of an S deficiency. About two to three weeks after plant emergence, a mild but general chlorosis appeared on the upper leaves of many plants growing in unamended Webster and Storden soils. The leaves turned a pale yellowish green color which can be characteristic of S deficiency (Wooding et al., 1970). The symptoms gradually intensified with time and also appeared on plants growing in the other two soils. At harvest, the upper leaves from plants growing in soils amended with low rates of S also exhibited similar symptoms.

From the soil test results in Table 1, all four soils are low in plant-available S (Voss, 1973). Tabatabai and Bremner (1972) reported that most Iowa soils are low in S. But this does not necessarily mean that plants grown on these soils will become S deficient since plants can absorb up to 30% of their S from the atmosphere as S gases such as

sulfur dioxide and hydrogen sulfide (Coleman, 1966). Under growth chamber conditions the air is filtered, and soybeans may become S deficient because air-borne S compounds are removed. Plants grown in pots may absorb less S from the soil because their roots are restricted to a smaller volume of soil than field-grown plants.

In this study the yield increase of 20% to S fertilization suggests that the S deficiency was mild. Beaton et al. (1971) considered a deficiency as marginal if S applications increased yields 5-10%. They considered the deficiency as severe if S fertilization increased yields 1000%. In this study low rates of either S source were equally effective in increasing dry matter yield (Table 19). Increasing rates of S application did not cause a proportionate increase in dry matter yield as shown in Appendix Table A20.

The dry matter yield increase of soybeans grown in S-amended Canisteo, Harps, Storden, and Webster soils was 42%, 23%, 8%, and 20%, respectively, compared to their controls (Table 19). Only the increase in yield from S-treated Canisteo soil was significant. The leaf concentration of S from plants grown on unamended Storden and Webster soils was 50% less than found in the S-treated plants (Table 19). The S amendments had little effect on the S concentration in the leaves of plants grown in Canisteo and Harps soil. The S treatments caused no significant differences in leaf Fe on any of the four soils. The dry matter yields and leaf tissue concentrations for all seven S treatments applied to all four soils are given in Appendix Table 21.

Dry matter yields from Storden and Webster soils were 30% and 17%

Table 19. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by S source and soil

S[b] source	S rate	DM[a] yield/ S source	Leaf tissue concentration/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
			Canisteo l					
C	0	1.8	0.29	1.65	0.17	87	37	44
ES	25, 50, 75	2.6*	0.31	1.68	0.19	93	42	38
PS	50, 100, 150	2.5*	0.32	1.69	0.17	111	42	38
			Harps l					
C	0	2.0	0.37	1.28	0.17	119	74	36
ES	25, 50, 75	2.4	0.41	1.26	0.17	120	100**	33
PS	50, 100, 150	2.5	0.41	1.31	0.20	108	97**	37
			Storden sl					
C	0	3.1	0.31	1.69	0.10	112	58	27
ES	25, 50, 75	3.4	0.36*	1.92	0.22**	132	86*	33
PS	50, 100, 150	3.3	0.37*	1.85	0.19**	141	71*	31
			Webster l					
C	0	2.5	0.30	1.86	0.11	114	54	45
ES	25, 50, 75	3.1	0.39*	1.97	0.22**	130	69	47
PS	50, 100, 150	2.9	0.36*	1.99	0.21**	115	58	45

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

*,**Significantly different from the control at the 5% and 1% level, respectively.

Table 20. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by soil, soil moisture, and temperature

Factors		DM[a] yield	Leaf tissue concentration					
			P	K	S	Fe	Mn	Zn
		g/pot	%			µg/g		
Soils								
Canisteo 1		2.4	0.31	1.68	0.18	99	41	39
Harps 1		2.4	0.40	1.28	0.19	115	95	35
Storden sl		3.4	0.36	1.86	0.19	133	76	31
Webster 1		3.0	0.36	1.96	0.20	121	62	46
Statistical evaluation[b]	1	**	ns	**	ns	**	ns	ns
	2	ns	**	**	ns	*	**	ns
	3	*	ns	ns	ns	ns	**	**
Soil water contents								
Medium soil water content		2.4	0.35	1.71	0.19	100	72**	41
High soil water content		3.1**	0.37	1.68	0.19	135**	64	34
Temperature								
25°C		2.7	0.35	1.66	0.18	118	69	39
30°C		2.8	0.36	1.73	0.19	116	68	36

[a]DM, dry matter.

[b]Statistical evaluation based on the following orthogonal comparisons:

1 Calcareous soil data vs Webster data
2 Canisteo data vs Harps data
3 Storden data vs Webster data.

*,**Significantly different at the 5% and 1% level, respectively; ns, not significant.

higher than yields from Canisteo and Harps soils which are prone to cause Fe deficiency, as shown in Table 20. Storden soil is generally considered a poor soil for crop production because its fertility is often low and its coarse texture (Table 1) limits its water-holding capacity. Storden soil contained more than double the amount of plant-available P compared to the other soils (Table 1). Storden soil also tested high in K. Under growth chamber conditions, where soil moisture is ample, such a coarse-textured soil high in P and K may promote better growth because of better fertility and better soil aeration. Under the high soil moisture regime, Storden soil significantly outyielded Webster soil by 21%. Under moderate moisture conditions, however, no differences in dry matter yield were noted between the two soils, as given in Table 21.

Soybean leaves harvested from plants grown in Canisteo soil contained 14% less Fe than those from Harps soil (Table 20). Leaves from plants grown in both soils contained 19% less Fe than those from Storden and Webster soils. The four soils did not significantly affect the S content of the leaves. The leaves of plants grown in Canisteo soil at moderate soil moisture contents contained 22% less Fe than those grown in Harps soil at the same moisture content. High moisture levels in Harps and Canisteo soils did not affect leaf Fe. Examination of individual plants grown in Canisteo soil at medium soil moisture revealed that several wilted due to severe moisture stress. The malformed leaves from these stunted plants were very low in Fe. The high soil moisture level increased plant dry

Table 21. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by soil at each soil moisture regime

Soil type		DM[a] yield	Leaf tissue concentration					
			P	K	S	Fe	Mn	Zn
		g/pot	%			μg/g		
Medium soil water content								
Canisteo 1		2.3	0.30	1.66	0.18	74	43	38
Harps 1		2.0	0.38	1.30	0.18	95	119	35
Storden sl		2.7	0.37	1.89	0.19	111	65	34
Webster 1		2.7	0.35	1.99	0.21	119	62	59
Statistical evaluation[b]	1	**	--	**	ns	**	**	ns
	2	--	**	--	--	*	**	--
	3	--	--	--	--	--	--	--
High soil water content								
Canisteo 1		2.6	0.33	1.70	0.17	125	39	40
Harps 1		2.7	0.42	1.26	0.20	135	70	34
Storden sl		4.0	0.35	1.82	0.19	155	86	29
Webster 1		3.3	0.37	1.93	0.20	123	61	33
Statistical evaluation	1	**	ns	**	ns	ns	**	*
	2	--	**	**	ns	--	--	--
	3	**	--	--	--	--	--	**

[a]DM, dry matter.

[b]Statistical evaluation based on orthogonal comparisons:

1 Calcareous soil data vs Webster data
2 Canisteo data vs Harps data
3 Storden data vs Webster data.

*,**Significantly different at the 5% and 1% level, respectively; ns, not significant.

matter yields 25% more and their leaf Fe content 35% more than those grown at medium soil moisture (Table 20). Increasing the temperature from 25°C to 30°C caused little increase in dry matter yield. The effect of temperature on plant growth for each soil at both temperatures is given in Appendix Table A22. The effect of temperature at each soil moisture level averaged over all the soils is shown in Table 22. A 5°C increase in temperature on plants growing in soils of medium soil moisture regime tended to decrease dry matter yields. This decrease may be due to a greater moisture stress placed on plants growing at the higher temperature. A 5°C increase in temperature and an increase in soil moisture increased dry matter yields 32%. In this experiment the most favorable conditions for plant growth occurred at the high soil moisture regime at 30°C.

S fertilization increased dry matter yields 28% compared to the controls at the medium soil moisture regime but only slightly at the high soil moisture regime as shown in Table 23. At high soil moisture, the controls contained 40% more dry matter than those at medium soil moisture. Applied S also increased the S content in the leaves 36% compared to the controls at both soil moisture levels. The leaves of plants grown in S-amended Webster and Storden soils contained twice the level of S at each moisture level as those grown in unamended controls (Tables 24 and 25). Applied S also increased dry matter yields at each temperature as shown in Table 26. S additions to each soil tended to increase the dry matter yield at each temperature regime except for plants grown on S-amended Storden at 25°C (Tables 27 and 28). None of the yield increases compared to the control was significant. S additions

Table 22. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by environmental factors

Environmental factors		DM[a] yield	Leaf tissue concentration					
Temp	SM[b] contents		P	K	S	Fe	Mn	Zn
		g/pot	%			µg/g		
25°C	Medium	2.5	0.35	1.66	0.19	94	72	42
25°C	High	3.0	0.36	1.66	0.18	141	65	37
30°C	Medium	2.3	0.36	1.77	0.19	105	73	41
30°C	High	3.3	0.37	1.70	0.20	128	63	31

[a]DM, dry matter.

[b]SM, soil moisture regime.

Table 23. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by S source and soil moisture

S[b] source	S rate	DM[a] yield/S source	Leaf tissue concentrations/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
			Medium soil water content					
C	0	2.0	0.31	1.67	0.14	94	57	42
ES	25, 50, 75	2.6*	0.36*	1.73	0.19**	98	79*	42
PS	50, 100, 150	2.5*	0.35*	1.71	0.19**	104	71*	41
			High soil water content					
C	0	2.8	0.32	1.57	0.14	122	55	34
ES	25, 50, 75	3.3	0.38**	1.69	0.20**	139	70	33
PS	50, 100, 150	3.1	0.37**	1.70	0.19**	134	62	35

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

*,**Significantly different from the control at the 5% and 1% level, respectively.

Table 24. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by S source and soil at moderate soil moisture

S[b] source	S rate	DM[a] yield/ S source	Leaf tissue concentration/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
			Canisteo l					
C	0	1.6	0.28	1.69	0.16	0.70	38	38
ES	25, 50, 75	2.4	0.29	1.68	0.19	0.74	46	37
PS	50, 100, 150	2.3	0.31	1.64	0.18	0.75	41	40
			Harps l					
C	0	1.6	0.36	1.37	0.16	96	89	32
ES	25, 50, 75	2.8	0.39	1.26	0.15	98	127**	33
PS	50, 100, 150	2.8	0.38	1.33	0.21	94	122**	40
			Storden sl					
C	0	2.5	0.31	1.64	0.09	96	45	33
ES	25, 50, 75	2.8	0.38	2.00	0.23**	96	75*	38
PS	50, 100, 150	2.8	0.38	1.88	0.18**	131	62*	30
			Webster l					
C	0	2.2	0.31	1.99	0.13	114	57	66
ES	25, 50, 75	2.8	0.38	1.98	0.24**	125	67	61
PS	50, 100, 150	2.7	0.35	2.02	0.20**	115	60	54

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

*,**Significantly different from the control at the 5% and 1% level, respectively.

Table 25. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by S source and soil at high soil moisture

S source[b]	S rate	DM[a] yield/ S source	Leaf tissue concentration/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
			Canisteo l					
C	0	2.0	0.29	1.61	0.18	105	37	50
ES	25, 50, 75	2.7	0.34	1.69	0.19	111	37	39
PS	50, 100, 150	2.7	0.33	1.76	0.15	147	42	37
			Harps l					
C	0	2.5	0.38	1.19	0.17	142	60	41
ES	25, 50, 75	2.6	0.42	1.27	0.20	143	73	33
PS	50, 100, 150	2.9	0.42	1.27	0.20	123	71	34
			Storden sl					
C	0	3.8	0.30	1.75	0.11	127	72	22
ES	25, 50, 75	4.2	0.36	1.85	0.21*	168	97	29
PS	50, 100, 150	3.9	0.35	1.83	0.19*	152	81	33
			Webster l					
C	0	2.8	0.30	1.73	0.10	114	51	24
ES	25, 50, 75	3.5	0.40*	1.97	0.21**	135	71	33
PS	50, 100, 150	3.2	0.37*	1.96	0.21**	115	55	36

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

*,**Significantly different from the control at the 5% and 1% level, respectively.

Table 26. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by S source at 25°C and 30°C

S Source[b]	S rate	DM[a] yield/ S source	Leaf tissue concentration/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
			25°C					
C	0	2.4	0.32	1.60	0.12	108	53	35
ES	25, 50, 75	2.8	0.37*	1.67	0.20**	118	74**	36
PS	50, 100, 150	2.8	0.35*	1.66	0.19**	121	68**	44
			30°C					
C	0	2.3	0.32	1.64	0.15	108	59	41
ES	25, 50, 75	3.0*	0.37*	1.75	0.21**	119	75*	39
PS	50, 100, 150	2.8*	0.37*	1.75	0.19**	117	65*	31

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

*,**Significantly different from the control at the 5% and 1% level, respectively.

Table 27. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by S source and soil at 25°C

S[b] source	S rate	DM[a] yield/ S source	Leaf tissue concentration/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
			Canisteo l					
C	0	1.8	0.34	1.79	0.18	101	35	47
ES	25, 50, 75	2.6	0.31	1.54	0.18	86	40	37
PS	50, 100, 150	2.5	0.31	1.64	0.14	113	43	39
			Harps l					
C	0	2.2	0.36	1.20	0.11	116	72	25
ES	25, 50, 75	2.4	0.42	1.21	0.12	137	99	30
PS	50, 100, 150	2.6	0.38	1.25	0.21	121	100	56
			Storden sl					
C	0	3.3	0.29	1.64	0.09	92	56	35
ES	25, 50, 75	3.2	0.39*	2.06	0.25**	126*	89*	38
PS	50, 100, 150	3.0	0.37*	1.90	0.21**	151*	78*	38
			Webster l					
C	0	2.5	0.28	1.77	0.11	123	51	34
ES	25, 50, 75	3.1	0.37*	1.88	0.24**	123	69	42
PS	50, 100, 150	3.1	0.34*	1.90	0.22**	101	53	44

[a]DM, dry matter.

[c]C, control; ES, elemental S; PS, pyrite S.

*,**Significantly different from the control at the 5% and 1% level, respectively.

Table 28. Dry matter yield and leaf tissue analyses of Wayne soybeans as affected by S source and soil at 30°C

S source[b]	S rate	DM[a] yield/ S source	Leaf tissue concentration/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
			Canisteo 1					
C	0	1.7	0.24	1.51	0.16	74	40	41
ES	25, 50, 75	2.5	0.33*	1.83	0.20	99	44	40
PS	50, 100, 150	2.6	0.33*	1.75	0.20	108	41	39
			Harps 1					
C	0	1.9	0.37	1.36	0.22	123	77	48
ES	25, 50, 75	2.5	0.40	1.32	0.23	104	102*	36
PS	50, 100, 150	2.4	0.43	1.35	0.21	96	93*	18
			Storden sl					
C	0	3.0	0.33	1.75	0.12	132	61	20
ES	25, 50, 75	3.8	0.34	1.79	0.19	139	84	29
PS	50, 100, 150	3.6	0.36	1.82	0.17	132	65	24
			Webster 1					
C	0	2.6	0.33	1.95	0.12	105	58	56
ES	25, 50, 75	3.2	0.41	2.06	0.22*	136	69	52
PS	50, 100, 150	2.8	0.38	2.08	0.20*	130	61	47

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

*,**Significantly different from the control at the 5% and 1% level, respectively.

averaged over all soils at each temperature increased the S content of the leaves 60% compared to the unamended controls. S additions to Storden and Webster soils doubled the S content of the leaves at both temperatures compared to those from the controls.

Second Growth Chamber Experiment

In this study only plants grown at high and moderate soil moisture regimes were analyzed because of the high mortality of plants grown at low soil moisture. The soybeans exhibited very mild Fe deficiency symptoms as the first trifoliate leaf developed, but these symptoms disappeared within two weeks. As in the first experiment, the C.I. data were not analyzed.

The AOV for the dry matter yield of the topgrowth and the nutrient composition (P, K, S, Fe, Mn, and Zn) of the leaves are given in Table 29. The AOV shows that differences due only to soil moisture level significantly affected dry matter yield. A comparison of the unamended control with the five pyrite-amended soils by means of an orthogonal comparison in Table 30 shows that the pyrite treatments increased the S content of the leaves 29% and increased the dry matter yield slightly but not significantly. Dry matter yields and nutrient leaf concentrations for individual treatments are listed in Appendix Table A23.

Pyrite had little effect on the concentration of Fe and Zn in the leaves (Table 30). The levels of all nutrients, except K, are sufficient in the leaves according to the critical nutrient ranges developed for more mature plants (Jones, 1966 and 1968; Kamprath et al., 1957).

Table 29. Analysis of variance of dry matter yield and leaf tissue analyses of Wayne soybean grown in Harps soil and affected by temperature, soil moisture, and pyrite

Source	d.f.	Mean squares						
		DM[a] yield	Leaf tissue analyses					
			P	K	S	Fe	Mn	Zn
Temp	1	0.72454	0.00567	0.15682	386081.0	322.7	121.5	805.0
Error a	0	0	0	0	0	0	0	0
H_2O	1	3.20470*	0.00956	0.18727	48.1	1290.7	5221.5*	70.0
Pyrite treatment	5	0.29561	0.00388	0.00683	353371.0	1211.7	313.3	150.0
H_2O*pyrite treatment	5	0.63219	0.00439	0.04517	21658.3	715.1	1004.9	284.6
Temp*H_2O	1	0.64354	0.00152	0.00167	111744.0	486.0	1536.0	18.4
Temp*pyrite treatment	5	0.69193	0.00215	0.01554	286535.9	414.7	1089.1	468.8
Error b	5	0.31957	0.00105	0.02957	63662.8	498.2	392.8	266.0
Total	23							
C.V.%		23.3	8.0	13.6	11.9	18.4	22.1	34.7

[a]DM, dry matter.

*Significant at the 5% level of probability.

Table 30. Dry matter yield and leaf tissue analyses of Wayne soybean grown in Harps soil as affected by pyrite

S[b] source	S rate	DM[a] yield/ S source	Leaf tissue concentration/S source					
			P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	——— % ———			——— µg/g ———		
C	0	2.0	0.37	1.28	0.17	120	74	36
PS	200, 400, 600 800, 1000	2.5	0.41	1.26	0.22**	121	93	35

[a]DM, dry matter.

[b]C, control; PS, pyrite S.

**Significantly different from the control at the 1% level.

Table 31. Dry matter yield and leaf tissue analyses of Wayne soybean grown on pyrite-amended Harps soil as affected by soil moisture and temperature

Environmental factors	DM[a] yield	Leaf tissue concentration					
		P	K	S	Fe	Mn	Zn
	g/pot	——— % ———			——— µg/g ———		
		Soil water contents					
Medium	2.1	0.42	1.36*	0.21	114	75	36
High	2.8*	0.38	1.18	0.21	129	105*	33
		Temperatures					
25°C	2.6	0.38	1.19	0.20	125	92	41
30°C	2.2	0.42	1.35	0.22	118	88	29

[a]DM, dry matter.

*Significant at the 5% level.

The younger leaves of many plants gradually turned a yellowish green color during the course of the experiment which may indicate S deficiency. Reasons for S deficiency in this experiment have been discussed previously. In this study low rates of pyrite were as effective as high rates in increasing the dry matter content of plants grown on Harps soil (Tables 19 and 30).

In both growth chamber experiments the high soil moisture regime increased dry matter yields 30% compared to plants grown at the moderate soil moisture regime (Tables 20 and 31). Plants grown in a growth chamber are more subject to moisture deficiency stress because the soil in a pot contains a limited amount of water and evapotranspiration rates may be very high. Greater moisture stress at 30°C may be responsible for the decrease in dry matter yield when compared to plants grown at 25°C as shown in Table 31. Increasing the temperature from 25° to 30° for plants growing in Harps soil at the medium moisture regime decreased dry matter yields 30% as shown in Table 32.

Table 32. Dry matter yield and leaf tissue analyses of Wayne soybean grown in pyrite-amended Harps soil and affected by environmental factors

Environmental factors		DM[a] yield	Leaf tissue concentration					
Temp	SM[b] content		P	K	S	Fe	Mn	Zn
		g/pot	%			µg/g		
25°C	Medium	2.4	0.41	1.27	0.19	122	114	41
25°C	High	2.8	0.36	1.11	0.21	128	69	40
30°C	Medium	1.7	0.43	1.45	0.23	106	94	32
30°C	High	2.8	0.40	1.20	0.22	129	80	26

[a]DM, dry matter.

[b]SM, soil moisture regime.

SUMMARY AND CONCLUSIONS

Wayne soybeans, a commercial cultivar, exhibited a 20% increase in dry matter yields and a 50% increase in S content in the leaves from either form of S applied at low rates (25-150 μg S/g soil) to all soils. Yield increases were significant only on S-amended Canisteo soil. Pyrite applied to Harps soil at low rates (50-150 μg S/g soil) and at high rates (200-1000 μg S/g soil) both increased dry matter yields 10%. The leaf S content associated with S-amended Storden and Webster soils was double that found in the leaves of unamended controls. Applications of either form of S did not adversely affect soybean growth at the rates used in this experiment.

Under growth chamber conditions, Wayne soybeans grown in calcareous, Fe deficient Canisteo and Harps soil did not become markedly Fe deficient. Mild symptoms of interveinal chlorosis appeared on the first trifoliate leaf as it developed, but these symptoms disappeared within two weeks. No deficiency symptoms were noted on plants grown in Storden and Canisteo soils. However, a mild pale yellow green chlorosis later appeared on the upper leaves of plants grown on the controls of all four soils. Such symptoms are characteristic of S deficiency. These results imply that elemental S and pyrite increased plant growth (dry matter yields) by correcting a S deficiency, rather than an Fe deficiency. Iowa soils are low in plant-available S, and this condition may have been aggravated in the growth chamber by the removal of S gases in the air through filtration. Additional experiments will be necessary to

determine if soybeans will respond to soil applications of either source of S in the field.

Under growth chamber conditions, soybeans grown in coarse-textured Storden soil outyielded those grown in the other three soils. This may be explained by better aeration of Storden soil, especially under conditions of ample soil moisture.

Soil moisture influenced plant growth much more than air temperature. At the low soil moisture regime, many plants suffered from severe moisture deficiency stress which caused severe wilting and drastically reduced dry matter yields. A few plants also wilted badly when subjected to moderate soil moisture levels at the higher temperature. The high soil moisture regime increased plant growth 30% more than plants growing at moderate soil moisture at either temperature. Optimum plant growth occurred on all soils containing high soil moisture levels at a temperature of 30°C. Because foliar symptoms of Fe and S deficiency were very mild, it was difficult to determine if temperature and soil moisture modified their expression.

SUMMARY AND CONCLUSIONS

The results of these three studies show that waste pyrite originating from Iowa coal may be of value as a source of plant-available Fe and S when applied in controlled amounts to Iowa soils.

The first study shows that waste pyrite contains relatively low contents of As, Pb, and Se. Oxidation of pyrite applied at 50-150 μg S/g in four soils and 1000 μg S/g Harps soil did not cause any detectable formation or accumulation of thiosulfate and tetrathionate compounds after incubation for two to six weeks. Because these potentially toxic substances are present in low or nondetectable levels, they are not likely to affect crop production. Pyrite treatments decreased soil pH by 0.3 units or less in this study.

The results of the second study show that elemental S and pyrite applied at 16 rates increasing from 0-5000 μg S/g soil to four soils decreased soil pH, increased DTPA-extractable Fe and Mn, and did not affect extractable Zn after 20 and 40 days incubation. Pyrite treatments decreased soil pH no more than 0.7 pH units regardless of soil type or incubation period, but elemental S decreased soil pH as much as 8 times more than pyrite treatments did. These results show that elemental S oxidation in soil produced greater acidity than pyrite.

An application of 2500 μg S as pyrite/g of highly calcareous Harps soil released quantities of Fe considered sufficient for plant growth, but twice that rate of elemental S did not. Similar rates of both S sources supplied adequate Fe to the moderately calcareous Storden soil.

For the slightly calcareous Canisteo soil, 250 µg S as elemental S/g soil and pyrite at 4 times that rate supplied adequate Fe. Both S sources applied to the slightly acid Webster soil released similar amounts of Fe after 20 days incubation, but pyrite supplied 50% more after 40 days.

A rate of 1000 µg S as elemental S/g soil decreased the pH of Canisteo soil sufficiently to supply Mn at levels considered sufficient for plant growth, but 5 times that rate of pyrite was required to do the same. Additions of elemental S at rates of 3000 µg S/g Canisteo soil or 1000 µg S/g Webster soil decreased the soil pH between 4.0-5.0 which may lead to Mn toxicity.

Pyrite and elemental S additions had little effect on the Zn content of soils partially as a result of previous Zn contamination. The Zn levels of the soils were highly correlated to their organic matter content. Storden soil contained one-third the Zn and one-half the organic matter content compared to the other soils.

Fe and Zn fixation may have occurred after incubating previously air-dry soils for 20 days. The Fe and Zn contents decreased an average of 43% and 28% in the four unamended soils. Doubling the incubation period further intensified Fe and Zn fixation in the three calcareous soils by causing a decrease in extractable Fe and Zn. The decreased DTPA-extractable Fe and Zn levels in calcareous soils with wetting and time of incubation may partially explain the frequent occurrence of Fe and Zn chlorosis under field conditions associated with prolonged wetting.

In unamended Webster soil, doubling the incubation period increased the Fe content to the air-dry value and increased the Zn content slightly. Because Fe fixation may have occurred in the unamended controls, it could be expected to influence extractable Fe from S-amended soils as well. This may explain why S-amended Canisteo and Storden soils at a given rate less than 250 µg S/g soil and why S-amended Harps soils at any given rate below 5000 µg S/g soil supplied less extractable Fe at 40 days incubation than at 20 days. Fe fixation may be temporary in S-amended Webster soil since the extractable Fe content increased much greater at 40 days incubation compared to the same treatments at 20 days.

In the growth chamber study, a commercial soybean cultivar, Wayne, exhibited a 20% increase in dry matter yields and a 50% increase in leaf S content from either form of S applied at low rates (25-150 µg S/g soil) to all soils. The soybeans probably responded to increased S levels in the S-amended soils, rather than increased Fe levels. The S treatments increased yields on all soil types, but only the yield increase of 40% associated with Canisteo soil was significant. Pyrite applied to Harps soil at low rates (50-150 µg S/g soil) and at high rates (200-1000 µg S/g soil) showed similar increases in yield. The S treatments doubled the leaf S content of plants grown in Storden and Webster soil compared to those grown in unamended controls.

Few symptoms of Fe deficiency were noted on soybeans grown in calcareous iron deficient Canisteo and Harps soil. Mild symptoms of chlorosis that appeared on the first trifoliate leaf as it matured disappeared

within two weeks. A mild pale yellowish green chlorosis, which is a symptom of S deficiency, later appeared on the upper leaves of plants grown in all unamended soils. These four soils tested low in plant-available S and this condition may have been aggravated in the growth chamber by removal of S gases in the air through filtration. Additional experiments will be necessary to determine whether soybeans can respond positively to soil applications of either S source in the field.

In this study soil moisture influenced plant growth much more than temperature. At low soil moisture, a number of plants wilted and died due to severe moisture stress. At a moderate soil moisture level, only a few wilted and died. The high soil moisture regime increased dry matter yields 30% more than plants grown under moderate soil moisture at either 25°C or 30°C. Optimum growth occurred on all soils at high soil moisture at 30°C. The symptoms of Fe and S deficiency were too mild to determine if their expression was modified by differences in soil moisture and temperature.

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APPENDIX

Table A1. Effect of elemental S on soil pH and DTPA-extractable Fe, Mn, and Zn in Canisteo soil after 20 and 40 days incubation at 25°C[a]

S rate	pH		Fe		Mn		Zn	
	20 days	40 days	20 days	40 days	20 days	40 days	20 days	40 days
µg/g soil			µg/g soil					
0	8.0	8.1	4.9	3.4	0.6	0.6	9.8	9.5
50	8.0	8.0	5.1	3.2	0.7	0.5	9.2	8.0
100	8.0	7.9	5.2	3.4	0.6	0.6	8.5	9.6
150	7.9	7.8	5.2	3.7	0.7	0.6	10.0	10.2
200	7.8	7.8	5.3	3.7	0.6	0.6	9.8	10.2
250	7.6	7.5	5.8	4.5	0.6	0.6	12.4	9.5
300	7.4	7.5	6.2	5.0	0.6	0.7	10.2	10.7
400	7.3	7.4	6.8	4.8	0.7	0.5	11.1	10.4
500	7.1	7.1	7.6	6.2	0.8	0.7	10.4	11.1
1000	6.6	6.6	10.0	10.0	1.1	1.1	11.4	11.4
1500	6.2	6.1	13.3	14.8	2.1	2.0	11.9	10.3
2000	5.7	5.7	17.3	21.3	4.6	4.7	10.4	12.3
2500	5.5	5.2	19.4	29.9	6.0	9.8	9.6	13.4
3000	5.2	5.0	24.4	37.5	10.1	17.5	9.1	14.1
4000	4.7	4.5	36.1	48.9	25.7	37.1	11.0	10.4
5000	4.4	4.4	41.1	54.9	35.1	40.3	12.2	11.3

[a]After 20 and 40 days of incubation, the pH was measured on field-moist (50% water-holding capacity) soil samples and Fe, Mn, and Zn were extracted with DTPA.

Table A2. Effect of pyrite on soil pH and DTPA-extractable Fe, Mn, and Zn in Canisteo soil after 20 and 40 days incubation at 25°C[a]

S rate	pH		Fe		Mn		Zn	
	20 days	40 days	20 days	40 days	20 days	40 days	20 days	40 days
µg/g soil			µg/g soil					
0	8.0	8.1	4.9	3.4	0.6	0.6	9.8	9.5
50	8.0	8.1	5.1	3.2	0.7	0.6	10.2	9.3
100	7.9	8.1	6.2	3.3	0.7	0.5	8.8	8.1
150	7.8	8.1	5.3	3.3	0.6	0.6	10.3	11.2
200	8.0	8.1	5.2	3.3	0.7	0.6	11.5	8.6
250	7.9	8.0	5.5	3.6	0.7	0.6	8.9	10.0
300	7.8	8.1	5.4	3.5	0.6	0.6	9.8	8.4
400	7.9	8.1	5.6	3.6	0.7	0.6	10.4	8.2
500	7.7	8.0	5.8	4.1	0.7	0.8	11.0	8.8
1000	7.9	8.0	6.5	4.5	0.8	0.6	10.5	9.8
1500	7.7	7.8	8.0	5.2	0.8	0.7	13.5	9.1
2000	7.8	7.8	8.0	5.9	0.7	0.7	10.6	10.4
2500	7.7	7.8	9.4	7.1	0.0	0.8	11.6	10.6
3000	7.8	7.7	9.4	7.8	0.9	0.8	14.5	9.8
4000	7.7	7.7	10.2	10.0	0.9	0.8	9.8	10.5
5000	7.7	7.5	11.5	12.9	1.0	0.8	10.9	12.0

[a]After 20 and 40 days of incubation, the pH was measured on field-moist (50% water-holding capacity) soil samples and Fe, Mn, and Zn were extracted with DTPA.

Table A3. Effect of elemental S on soil pH and DTPA-extractable Fe, Mn, and Zn in Harps soil after 20 and 40 days incubation at 25°C[a]

S rate	pH		Fe		Mn		Zn	
	20 days	40 days	20 days	40 days	20 days	40 days	20 days	40 days
µg/g soil			µg/g soil					
0	8.4	8.5	1.8	0.9	1.2	1.2	13.0	9.6
50	8.3	8.4	1.5	0.9	1.2	1.1	13.0	10.9
100	8.1	8.2	1.5	0.9	1.1	1.1	11.8	11.2
150	8.1	8.0	1.6	1.4	1.4	1.0	13.6	13.1
200	8.0	8.2	1.8	0.8	1.1	1.1	11.9	10.7
250	7.8	7.9	1.8	1.1	1.0	0.9	10.8	13.5
300	7.9	8.0	1.9	1.0	1.0	0.9	11.6	10.1
400	7.8	7.9	1.7	1.1	0.4	0.9	14.4	11.3
500	7.6	7.9	1.9	1.6	0.8	0.9	13.6	10.1
1000	7.6	7.6	1.9	1.4	0.9	0.8	14.0	11.9
1500	7.6	7.8	2.2	1.2	0.9	0.9	13.7	12.0
2000	7.5	7.6	2.1	1.4	0.9	0.8	14.9	10.9
2500	7.6	7.7	2.2	1.4	1.1	0.9	14.2	12.7
3000	7.4	7.5	2.4	1.8	1.1	0.8	14.0	16.7
4000	7.4	7.3	2.8	2.0	1.3	0.9	11.2	11.1
5000	7.3	7.4	3.2	2.2	1.5	1.0	13.3	13.1

[a]After 20 and 40 days of incubation, the pH was measured on field-moist (50% water-holding capacity) soil samples and Fe, Mn, and Zn were extracted with DTPA.

Table A4. Effect of pyrite on soil pH and DTPA-extractable Fe, Mn, and Zn in Harps soil after 20 and 40 days incubation at 25°C[a]

S rate	pH		Fe		Mn		Zn	
	20 days	40 days	20 days	40 days	20 days	40 days	20 days	40 days
µg/g soil			µg/g soil					
0	8.4	8.5	1.8	0.9	1.2	1.2	13.0	9.6
50	8.5	8.5	1.7	1.9	1.4	1.1	17.0	10.0
100	8.3	8.4	1.5	1.0	1.1	1.2	13.3	10.1
150	8.3	8.5	1.5	0.8	1.1	1.0	13.6	9.1
200	8.3	8.4	2.0	1.0	1.2	1.0	11.4	9.6
250	8.3	8.5	1.6	1.0	1.1	1.1	11.7	9.4
300	8.4	8.5	1.7	1.1	1.1	1.1	11.8	11.8
400	8.2	8.3	2.0	1.2	1.1	1.1	15.7	10.5
500	8.3	8.5	2.1	1.3	1.2	1.2	13.7	11.1
1000	8.3	8.0	2.5	2.4	1.3	1.3	14.9	14.7
1500	8.0	8.0	3.5	3.0	1.3	1.3	11.2	10.2
2000	8.0	8.0	4.6	3.9	1.5	1.4	14.5	10.3
2500	8.0	7.9	4.8	4.5	1.6	1.4	13.2	10.0
3000	8.0	7.9	5.5	5.2	1.6	1.4	11.8	13.3
4000	7.9	8.0	7.5	5.9	1.8	1.4	13.7	12.7
5000	8.0	7.8	8.5	7.8	1.7	1.4	13.3	11.9

[a]After 20 and 40 days of incubation, the pH was measured on field-moist (50% water-holding capacity) soil samples and Fe, Mn, and Zn were extracted with DTPA.

Table A5. Effect of elemental S on soil pH and DTPA-extractable Fe, Mn, and Zn in Storden soil after 20 and 40 days incubation at 25°C[a]

S rate	pH		Fe		Mn		Zn	
	20 days	40 days	20 days	40 days	20 days	40 days	20 days	40 days
µg/g soil			µg/g soil					
0	7.7	7.8	4.3	3.0	1.3	1.1	3.1	2.7
50	7.7	7.7	4.3	3.1	1.2	1.1	2.8	2.4
100	7.5	7.7	4.3	3.2	1.1	1.0	3.4	2.7
150	7.5	7.6	4.5	3.0	1.1	0.9	2.6	2.8
200	7.5	7.6	4.3	2.8	1.1	1.0	2.4	2.5
250	7.5	7.7	4.4	2.8	1.1	1.0	2.7	2.0
300	7.5	7.6	4.3	3.3	1.2	1.0	1.7	2.0
400	7.5	7.4	4.3	3.3	1.2	1.0	2.4	2.3
500	7.4	7.3	4.3	3.6	1.2	1.1	2.4	3.2
1000	7.3	7.2	4.4	4.2	1.5	1.1	2.3	2.4
1500	7.1	7.0	4.9	4.6	4.1	1.8	2.3	3.0
2000	7.1	6.8	5.0	5.8	7.0	2.0	2.3	2.7
2500	7.0	6.4	5.3	6.4	31.2	27.9	2.8	2.7
3000	6.7	6.4	6.5	8.3	23.5	25.0	2.6	3.8
4000	7.3	5.9	4.7	10.4	30.6	35.0	2.4	2.6
5000	7.2	5.4	4.8	15.8	36.3	34.4	3.0	3.4

[a]After 20 and 40 days of incubation, the pH was measured on field-moist (50% water-holding capacity) soil samples and Fe, Mn, and Zn were extracted with DTPA.

Table A6. Effect of pyrite on soil pH and DTPA-extractable Fe, Mn, and Zn in Storden soil after 20 and 40 days incubation at 25°C[a]

S rate	pH		Fe		Mn		Zn	
	20 days	40 days	20 days	40 days	20 days	40 days	20 days	40 days
µg/g soil			µg/g soil					
0	7.7	7.8	4.3	3.0	1.3	1.1	3.1	2.7
50	7.6	7.7	4.0	3.3	1.2	1.2	2.9	2.7
100	7.5	7.7	4.3	3.2	1.5	1.1	2.5	3.3
150	7.6	7.7	4.6	3.1	1.3	1.1	2.4	2.7
200	7.5	7.7	5.1	3.5	1.4	1.2	2.3	2.1
250	7.6	7.9	4.6	3.2	1.4	1.3	2.9	4.3
300	7.5	7.6	5.2	3.8	1.5	1.2	3.2	2.9
400	7.5	7.6	5.0	4.0	1.4	1.3	2.6	2.4
500	7.6	7.8	5.1	3.8	1.5	1.4	2.3	2.5
1000	7.5	7.7	6.8	4.7	1.5	1.3	3.7	2.6
1500	7.6	7.7	6.9	7.0	1.6	2.4	3.2	3.4
2000	7.5	7.6	8.4	6.2	1.8	1.5	2.5	2.3
2500	7.5	7.7	8.5	7.5	2.0	1.7	2.8	5.0
3000	7.5	7.6	9.6	9.9	2.1	1.9	3.5	2.6
4000	7.5	7.4	11.0	13.4	2.5	2.2	3.0	3.2
5000	7.5	7.5	12.3	13.4	2.8	2.3	3.7	4.5

[a]After 20 and 40 days of incubation, the pH was measured on field-moist (50% water-holding capacity) soil samples and Fe, Mn, and Zn were extracted with DTPA.

Table A7. Effect of elemental S on soil pH and DTPA-extractable Fe, Mn, and Zn in Webster soil after 20 and 40 days incubation at 25°C[a]

S rate	pH		Fe		Mn		Zn	
	20 days	40 days	20 days	40 days	20 days	40 days	20 days	40 days
µg/g soil			µg/g soil					
0	6.1	6.1	56.4	84.0	2.7	2.6	11.9	12.6
50	6.0	5.9	56.9	82.1	2.6	2.6	12.8	15.3
100	5.8	5.8	57.7	85.7	3.1	3.2	12.3	13.6
150	5.7	5.7	61.6	91.0	3.7	3.5	9.0	13.8
200	5.6	5.6	62.6	94.0	3.6	3.8	8.9	11.8
250	5.6	5.4	62.7	93.1	3.9	3.8	10.1	12.8
300	5.5	5.4	65.1	99.1	4.3	5.4	7.9	11.6
400	5.4	5.2	63.8	99.4	5.1	5.0	8.5	13.1
500	5.3	5.1	62.9	101.6	5.9	6.7	8.7	12.9
1000	4.9	4.6	77.5	118.8	18.0	32.4	7.7	12.2
1500	5.0	4.4	79.7	129.2	32.0	59.9	8.2	15.0
2000	4.9	4.2	82.9	142.0	40.5	83.0	11.2	12.8
2500	4.8	3.9	83.7	158.2	49.1	103.5	10.6	11.0
3000	4.7	3.8	90.0	165.7	57.5	110.9	8.5	12.1
4000	4.7	3.9	89.4	151.9	57.4	100.7	9.0	13.4
5000	4.8	3.8	99.0	163.6	65.1	114.1	10.2	12.6

[a]After 20 and 40 days of incubation, the pH was measured on field-moist (50% water-holding capacity) soil samples and Fe, Mn, and Zn were extracted with DTPA.

Table A8. Effect of pyrite on soil pH and DTPA-extractable Fe, Mn, and Zn in Webster soil after 20 and 40 days incubation at 25°C[a]

S rate	pH		Fe		Mn		Zn	
	20 days	40 days	20 days	40 days	20 days	40 days	20 days	40 days
µg/g soil			µg/g soil					
0	6.1	6.1	56.4	84.0	2.7	2.6	11.9	12.6
50	6.2	6.1	59.1	85.8	2.9	2.8	9.5	15.3
100	6.2	6.1	59.5	87.0	2.6	3.0	8.2	15.6
150	6.2	6.1	60.0	87.7	2.7	2.8	8.6	12.4
200	6.2	6.0	60.3	86.5	2.7	2.7	9.7	14.4
250	6.2	6.0	63.6	91.7	2.6	2.7	9.0	12.7
300	6.2	6.0	64.2	96.0	2.8	2.7	8.4	13.6
400	6.2	6.0	69.7	104.0	3.0	2.9	10.3	15.5
500	6.2	5.9	66.9	106.4	2.8	2.9	12.0	13.2
1000	6.2	5.7	71.6	178.4	3.2	3.6	9.8	13.6
1500	6.2	5.6	76.1	194.3	3.6	3.6	9.9	10.8
2000	6.2	5.6	78.7	203.1	3.8	3.9	9.7	13.8
2500	6.1	5.5	84.3	248.5	4.0	4.7	9.8	15.2
3000	6.1	5.5	87.2	262.5	4.2	4.8	10.9	13.9
4000	6.1	5.6	87.4	254.8	4.8	5.1	9.3	12.6
5000	6.1	5.6	87.4	253.4	5.1	5.4	10.2	15.8

[a]After 20 and 40 days of incubation, the pH was measured on field-moist (50% water-holding capacity) soil samples and Fe, Mn, and Zn were extracted with DTPA.

Table A9. Effect of elemental S and pyrite on DTPA-extractable Fe, Mn, and Zn in four unincubated, air-dry soils

S rate	pH	S source					
		Elemental S			Pyrite		
		Fe	Mn	Zn	Fe	Mn	Zn
µg/g soil		µg/g soil					
		Canisteo l					
0	7.7	10.8	11.0	14.3	10.8	11.0	14.3
250	--	10.9	10.5	9.4	11.5	10.9	12.9
500	--	10.9	10.4	8.5	14.3	10.9	12.5
1000	--	11.3	10.8	13.3	14.1	11.7	12.7
2500	--	11.0	10.9	11.7	14.0	13.1	16.6
5000	--	11.3	10.3	10.7	16.2	14.0	14.0
		Harps l					
0	8.3	4.4	10.4	17.8	4.4	10.4	17.8
250	--	4.5	10.8	12.9	5.0	9.0	5.9
500	--	4.5	12.4	17.5	5.1	8.8	6.8
1000	--	4.8	13.3	21.2	6.7	8.7	9.2
2500	--	5.0	12.9	17.3	7.3	10.5	6.2
5000	--	4.8	13.0	23.3	10.4	12.9	7.9
		Storden sl					
0	7.8	5.9	1.2	4.1	5.9	1.2	4.1
250	--	6.0	1.3	3.9	6.3	1.3	4.0
500	--	5.8	1.2	5.9	7.8	1.3	4.8
1000	--	6.1	1.3	5.4	8.2	1.4	4.1
2500	--	6.2	1.4	4.7	8.6	1.5	4.3
5000	--	6.1	1.3	3.9	11.0	1.5	5.1
		Webster l					
0	6.2	83.4	2.5	17.3	83.4	2.5	17.3
250	--	86.9	2.6	15.8	88.3	2.5	15.4
500	--	85.0	2.5	19.5	91.4	2.6	16.0
1000	--	85.3	2.3	19.5	96.1	2.5	18.9
2500	--	81.2	2.4	17.5	90.8	2.7	21.5
5000	--	87.9	2.5	18.0	94.8	2.9	19.1

Table A10. pH and DTPA-extractable Fe, Mn, and Zn of all soils as affected by four two-factor and four three-factor interactions

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			μg/g soil		
IP*SS					
20 day*PS	60	7.4	22.2	1.8	9.3
20 day*ES	60	6.7	23.4	10.1	8.9
40 day*PS	60	7.4	42.5	1.8	9.4
40 day*ES	60	6.6	35.5	15.0	9.6
Soil*SR[b]					
Canisteo*50	4	8.0	4.0	1.0	9.0
*100	4	8.0	4.3	1.0	8.8
*150	4	7.9	4.3	1.0	10.3
*200	4	7.9	4.3	1.0	10.3
*250	4	7.8	4.8	1.0	10.3
*300	4	7.7	5.0	1.0	9.8
*400	4	7.7	5.5	1.0	9.8
*500	4	7.5	6.0	1.0	10.3
*1000	4	7.3	8.0	1.0	10.5
*1500	4	7.0	10.3	1.5	11.3
*2000	4	6.7	13.3	3.0	10.8
*2500	4	6.6	16.3	4.5	11.5
*3000	4	6.4	19.8	7.5	11.8
*4000	4	6.2	26.3	16.3	10.5
*5000	4	6.0	30.0	19.3	11.5
Harps*50	4	8.4	1.3	1.0	12.8
*100	4	8.3	1.3	1.0	11.5
*150	4	8.2	1.5	1.0	12.5
*200	4	8.2	1.5	1.0	10.8
*250	4	8.1	1.5	1.0	11.3
*300	4	8.2	1.5	1.0	11.5
*400	4	8.1	1.5	1.0	13.0
*500	4	8.1	1.8	1.0	12.3
*1000	4	7.9	1.8	1.0	13.8
*1500	4	7.9	2.3	1.0	11.8
*2000	4	7.8	2.8	1.0	12.8
*2500	4	7.8	3.0	1.3	12.5
*3000	4	7.7	3.5	1.3	14.0
*4000	4	7.7	4.8	1.3	12.3
*5000	4	7.6	5.3	1.5	12.8

[a]IP, incubation period; SS, sulfur source; SR, sulfur rate; PS, pyrite rate; ES, elemental sulfur.

[b]μg S/g soil.

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
Storden*50	4	7.7	3.5	1.0	2.8
*100	4	7.6	3.5	1.0	3.0
*150	4	7.6	4.0	1.0	2.8
*200	4	7.6	3.8	1.0	2.3
*250	4	7.7	3.8	1.0	3.0
*300	4	7.5	4.0	1.0	2.5
*400	4	7.5	4.3	1.3	2.3
*500	4	7.5	4.3	1.3	2.3
*1000	4	7.4	5.0	1.5	2.8
*1500	4	7.4	6.0	2.5	2.8
*2000	4	7.3	6.3	3.3	2.5
*2500	4	7.2	6.5	15.8	3.5
*3000	4	7.1	8.5	13.3	3.5
*4000	4	7.0	9.8	17.5	2.8
*5000	4	6.9	11.5	18.3	3.5
Soil*SR[b]					
Webster*50	4	6.1	71.0	3.0	13.0
*100	4	6.0	72.5	3.0	12.5
*150	4	5.9	75.2	3.5	11.0
*200	4	5.9	75.7	3.5	11.3
*250	4	5.8	78.0	3.5	11.3
*300	4	5.8	81.0	3.8	10.8
*400	4	5.7	84.3	4.3	12.0
*500	4	5.6	84.7	4.8	11.8
*1000	4	5.4	111.5	14.3	11.0
*1500	4	5.3	119.8	24.8	11.0
*2000	4	5.2	127.0	30.5	12.0
*2500	4	5.1	143.5	40.3	11.8
*3000	4	5.0	151.5	44.3	11.3
*4000	4	5.1	145.8	42.0	11.0
*50000	4	5.1	151.0	47.3	12.0
IP*SR[b]					
20 day*50	8	7.5	17.1	1.5	9.6
*100	8	7.4	17.4	1.5	8.5
*150	8	7.4	18.3	1.6	8.9
*200	8	7.4	18.3	1.6	8.5
*250	8	7.3	18.9	1.6	8.6
*300	8	7.3	19.1	1.6	8.3
*400	8	7.2	20.0	1.8	9.4

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*500	8	7.2	19.6	2.0	9.3
*1000	8	7.0	22.6	3.6	9.3
*1500	8	6.9	24.3	5.8	9.4
*2000	8	6.8	25.9	7.6	9.4
*2500	8	6.8	27.0	12.0	9.5
*3000	8	6.7	24.3	12.6	9.4
*4000	8	6.7	31.1	15.6	8.6
*5000	8	6.6	33.4	18.6	9.5
40 days*50	8	7.6	22.8	1.5	9.1
*100	8	7.5	23.4	1.5	9.4
*150	8	7.4	24.3	1.6	9.4
*200	8	7.4	24.4	1.6	8.8
*250	8	7.4	25.1	1.6	9.3
*300	8	7.3	26.6	1.8	9.0
*400	8	7.2	27.6	1.9	9.1
*500	8	7.2	28.8	2.0	9.8
*1000	8	7.0	40.5	5.3	9.0
*1500	8	6.8	44.9	9.1	9.6
*2000	8	6.7	48.8	11.3	10.1
*2500	8	6.5	57.6	18.9	10.9
*3000	8	6.4	62.4	20.5	9.6
*4000	8	6.3	62.1	22.9	10.4
*5000	8	6.2	65.5	24.5	
SS*SR[b]					
PS*50	8	7.6	20.4	1.5	9.5
*100	8	7.5	20.6	1.5	8.8
*150	8	7.5	20.9	1.5	8.8
*200	8	7.5	20.6	1.5	8.6
*250	8	7.6	22.0	1.5	8.6
*300	8	7.6	22.6	1.5	8.9
*400	8	7.5	24.5	1.5	9.5
*500	8	7.5	24.5	1.6	9.3
*1000	8	7.4	34.8	1.8	10.0
*1500	8	7.3	37.9	1.9	8.9
*2000	8	7.3	39.8	2.0	9.3
*2500	8	7.3	46.5	2.3	9.9
*3000	8	7.3	49.6	2.3	10.1
*4000	8	7.2	50.0	2.4	9.5
*5000	8	7.2	50.8	2.5	10.1

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
ES*50	8	7.5	19.5	1.5	9.3
*100	8	7.4	20.1	1.5	9.1
*150	8	7.3	21.6	1.8	9.5
*200	8	7.3	22.0	1.8	8.6
*250	8	7.1	22.0	1.8	9.3
*300	8	7.1	23.1	1.9	8.4
*400	8	7.0	23.1	2.1	9.0
*500	8	6.9	23.9	2.4	9.0
*1000	8	6.6	28.4	7.1	9.0
*1500	8	6.4	31.3	13.0	9.5
*2000	8	6.2	34.9	16.9	9.8
*2500	8	6.0	38.1	28.6	9.8
*3000	8	5.8	42.0	30.9	10.1
*4000	8	5.7	43.3	36.1	8.8
*5000	8	5.6	48.1	40.6	9.8
Soil*SS*SR[b]					
Canisteo*PS					
*50	2	8.1	4.0	1.0	9.5
*100	2	8.0	4.5	1.0	8.5
*150	2	8.0	4.0	1.0	10.5
*200	2	8.1	4.0	1.0	10.5
*250	2	8.0	4.5	1.0	9.5
*300	2	8.0	4.5	1.0	9.0
*400	2	8.0	5.0	1.0	9.0
*500	2	7.9	5.0	1.0	10.0
*1000	2	8.0	6.0	1.0	10.0
*1500	2	7.8	6.5	1.0	11.5
*2000	2	7.8	7.0	1.0	10.5
*2500	2	7.8	8.0	1.0	11.5
*3000	2	7.8	8.5	1.0	12.0
*4000	2	7.7	10.0	1.0	10.5
*5000	2	7.6	12.0	1.0	11.5
*ES*50	2	8.0	4.0	1.0	8.5
*100	2	8.0	4.0	1.0	9.0
*150	2	7.9	4.5	1.0	10.0
*200	2	7.8	4.5	1.0	10.0
*250	2	7.6	5.0	1.0	11.0
*300	2	7.4	5.5	1.0	10.5
*400	2	7.4	6.0	1.0	10.5
*500	2	7.2	7.0	1.0	10.5

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			μg/g soil		
*1000	2	6.6	10.0	1.0	11.0
*1500	2	6.2	14.0	2.0	11.0
*2000	2	5.7	19.5	5.0	11.0
*2500	2	5.4	24.5	8.0	11.5
*3000	2	5.1	31.0	14.0	11.5
*4000	2	4.6	42.5	31.5	10.5
*5000	2	4.4	48.0	37.5	11.5
Harps*PS*50	2	8.5	1.5	1.0	13.5
*100	2	8.4	1.5	1.0	11.5
*150	2	8.4	1.5	1.0	11.5
*200	2	8.4	1.5	1.0	10.0
*250	2	8.4	1.5	1.0	10.5
*300	2	8.5	1.5	1.0	12.0
*400	2	8.3	1.5	1.0	13.5
*500	2	8.4	1.5	1.0	12.5
*1000	2	8.2	2.0	1.0	14.5
*1500	2	8.0	3.0	1.0	10.5
*2000	2	8.0	4.0	1.0	12.0
*2500	2	8.0	4.5	1.5	11.5
*3000	2	8.0	5.0	1.5	12.5
*3000	2	8.0	5.0	1.5	12.5
*4000	2	8.0	7.0	1.5	13.5
*5000	2	7.9	8.0	1.5	12.5
Soil*SS*SR[b]					
Harps*ES*50	2	8.4	1.0	1.0	12.0
*100	2	8.2	1.0	1.0	11.5
*150	2	8.1	1.5	1.0	13.5
*200	2	8.1	1.5	1.0	11.5
*250	2	7.9	1.5	1.0	12.0
*300	2	8.0	1.5	1.0	11.0
*400	2	7.9	1.5	1.0	12.5
*500	2	7.8	2.0	1.0	12.0
*1000	2	7.6	1.5	1.0	13.0
*1500	2	7.7	1.5	1.0	13.0
*2000	2	7.6	1.5	1.0	13.5
*2500	2	7.7	1.5	1.0	13.5
*3000	2	7.5	2.0	1.0	15.5
*4000	2	7.4	2.5	1.0	11.0
*5000	2	7.4	2.5	1.5	13.0

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			μg/g soil		
Storden*PS					
*50	2	7.7	3.5	1.0	2.5
*100	2	7.6	3.5	1.0	3.0
*150	2	7.7	4.0	1.0	3.0
*200	2	7.6	4.0	1.0	2.5
*250	2	7.8	4.0	1.0	2.0
*300	2	7.4	4.5	1.0	3.5
*400	2	7.6	4.5	1.0	3.0
*500	2	7.7	4.5	1.5	2.0
*1000	2	7.6	6.0	1.5	2.0
*1500	2	7.7	7.0	2.0	3.0
*2000	2	7.6	7.0	2.0	2.5
*2500	2	7.6	7.5	2.0	4.0
*3000	2	7.6	10.0	2.0	3.5
*4000	2	7.5	12.0	2.0	3.0
*5000	2	7.5	12.5	2.5	4.0
Storden*ES					
*50	2	7.7	3.5	1.0	2.5
*100	2	7.6	3.5	1.0	3.0
*150	2	7.6	4.0	1.0	3.0
*200	2	7.6	3.5	1.0	2.5
*250	2	7.6	3.5	1.0	2.5
*300	2	7.6	3.5	1.0	2.0
*400	2	7.5	3.5	1.0	2.0
*500	2	7.4	4.0	1.0	2.5
*1000	2	7.3	4.0	1.5	2.0
*1500	2	7.1	5.0	3.0	2.5
*2000	2	7.0	5.5	4.5	2.5
*2500	2	6.7	5.5	29.5	3.0
*3000	2	6.6	7.0	24.5	3.5
*4000	2	6.6	7.5	33.0	2.5
*5000	2	6.3	10.5	34.0	3.0
Soil*SS*SR[b]					
Webster*PS					
*50	2	6.2	72.5	3.0	12.0
*100	2	6.2	73.0	3.0	12.0
*150	2	6.2	74.0	3.0	10.5
*200	2	6.1	73.0	3.0	12.0
*250	2	6.1	78.0	3.0	11.0
*300	2	6.1	80.0	3.0	11.5
*400	2	6.1	87.0	3.0	13.0

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*500	2	6.1	87.0	3.0	12.5
*1000	2	6.0	125.0	3.5	12.0
*1500	2	5.9	135.0	3.5	10.5
*2000	2	5.9	141.0	4.0	12.0
*2500	2	5.8	166.0	4.5	12.5
*3000	2	5.8	175.0	4.5	12.5
*4000	2	5.9	171.0	5.0	11.0
*5000	2	5.9	170.5	5.0	12.5
Webster*ES					
*50	2	6.0	69.5	3.0	14.0
*100	2	5.8	72.0	3.0	13.0
*150	2	5.7	76.5	4.0	11.5
*200	2	5.6	78.5	4.0	10.5
*250	2	5.5	78.0	4.0	11.5
*300	2	5.5	82.0	4.5	10.0
*400	2	5.3	81.5	5.5	11.0
*500	2	5.2	82.5	6.5	11.0
*1000	2	4.8	98.0	25.0	10.0
*1500	2	4.7	104.5	46.0	11.5
*2000	2	4.6	113.0	57.0	12.0
*2500	2	4.4	121.0	76.0	11.0
*3000	2	4.3	128.0	84.0	10.0
*4000	2	4.3	120.5	79.0	11.0
*5000	2	4.3	131.5	89.5	11.5
Soil*IP*SS					
Canisteo*20 day					
*PS	15	7.7	7.0	1.0	10.9
*20 day*ES	15	6.6	13.9	6.2	10.3
*40 day*PS	15	7.9	5.5	1.0	9.7
*40 day*ES	15	6.6	16.7	8.1	10.7
Harps*20 day					
*PS	15	8.2	3.4	1.3	13.4
*20 day*ES	15	7.7	2.0	1.1	13.1
*40 day*PS	15	8.2	2.7	1.0	10.9
*40 day*ES	15	7.8	1.3	1.0	12.0
Storden*20 day					
*PS	15	7.5	6.7	1.6	3.0
*20 day*ES	15	7.3	4.5	9.5	2.5
*40 day*PS	15	7.7	5.9	1.4	3.0
*40 day*ES	15	7.1	5.3	8.9	2.7

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			μg/g soil		
Webster*20 day					
*PS	15	6.2	71.7	3.5	9.7
*20 day*ES	15	5.3	73.1	23.4	9.6
*40 day*PS	15	5.8	156.0	3.7	13.9
*40 day*ES	15	4.9	118.5	42.1	13.0
IP*SS*SR[b]					
20 day*PS					
*50	4	7.6	17.5	1.5	9.8
*100	4	7.5	17.8	1.5	8.3
*150	4	7.5	18.0	1.5	8.8
*200	4	7.5	18.0	1.5	8.8
*250	4	7.5	19.0	1.5	8.3
*300	4	7.5	19.0	1.5	8.5
*400	4	7.5	20.8	1.5	9.8
*500	4	7.5	20.0	1.8	9.8
*1000	4	7.5	22.0	1.8	9.8
*1500	4	7.4	23.5	1.8	9.5
*2000	4	7.4	24.8	2.0	9.5
*2500	4	7.3	26.5	2.3	9.5
*3000	4	7.4	27.8	2.3	9.3
*4000	4	7.3	29.0	2.5	9.0
*5000	4	7.3	29.8	2.8	9.5
*ES*50	4	7.5	16.8	1.5	9.5
*100	4	7.4	17.0	1.5	8.8
*150	4	7.3	18.5	1.8	9.0
*200	4	7.2	18.5	1.8	8.3
*250	4	7.1	18.8	1.8	9.0
*300	4	7.1	19.3	1.8	8.0
*400	4	7.8	19.3	2.0	9.0
*500	4	6.9	19.3	2.3	8.8
*1000	4	6.6	23.3	5.5	8.8
*1500	4	6.5	25.0	9.8	9.3
*2000	4	6.3	27.0	13.3	9.3
*2500	4	6.2	27.5	21.8	9.5
*3000	4	6.0	30.8	23.0	8.5
*4000	4	6.0	33.3	28.8	8.3
*5000	4	5.9	37.0	34.5	9.5
40 day*PS*50	4	7.6	23.3	1.5	9.3
*100	4	7.6	23.5	1.5	9.3
*150	4	7.6	23.8	1.5	8.8
*200	4	7.6	23.3	1.5	8.5

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*250	4	7.6	25.0	1.5	9.0
*300	4	7.6	26.3	1.5	9.3
*400	4	7.5	28.3	1.5	9.3
*500	4	7.6	29.0	1.5	8.8
*1000	4	7.4	47.5	1.8	10.3
*1500	4	7.3	52.3	2.0	8.3
*2000	4	7.3	54.8	2.0	9.0
*2500	4	7.2	66.5	2.3	10.3
*3000	4	7.2	71.5	2.3	10.0
*4000	4	7.2	71.0	2.3	10.0
*5000	4	7.1	71.8	2.3	10.8
IP*SS*SR[b]					
40 day*ES*50	4	7.5	22.3	1.5	9.0
*100	4	7.4	23.3	1.5	9.5
*150	4	7.3	24.8	1.8	10.0
*200	4	7.3	25.5	1.8	9.0
*250	4	7.1	25.3	1.8	9.5
*300	4	7.1	27.0	2.0	8.8
*400	4	7.0	27.0	2.3	9.0
*500	4	6.8	28.5	2.5	9.3
*1000	4	6.5	33.5	8.8	9.3
*1500	4	6.3	37.5	16.3	9.8
*2000	4	6.1	42.8	20.5	10.3
*2500	4	5.8	48.8	35.5	10.0
*2500	4	5.8	48.8	35.5	10.0
*3000	4	5.7	53.3	38.8	11.8
*4000	4	5.4	53.3	43.5	9.3
*5000	4	5.3	59.3	46.8	10.0
Soil*IP*SR[b]					
Canisteo*20 day					
*50	2	8.0	5.0	1.0	9.5
*100	2	8.0	5.5	1.0	8.5
*150	2	7.9	5.0	1.0	10.0
*200	2	8.0	5.0	1.0	11.0
*250	2	7.9	5.5	1.0	10.5
*300	2	7.6	5.5	1.0	10.0
*400	2	7.6	6.5	1.0	10.5
*500	2	7.4	7.0	1.0	10.5
*1000	2	7.3	8.5	1.0	10.5
*1500	2	6.9	10.5	1.5	13.0
*2000	2	6.8	13.0	3.0	10.5

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*2500	2	6.6	14.0	3.5	11.0
*3000	2	6.5	17.0	5.5	11.5
*4000	2	6.2	23.0	13.5	10.5
*5000	2	6.1	26.0	18.0	11.5
*40 day*50	2	8.1	3.0	1.0	8.5
*100	2	8.0	3.0	1.0	9.0
*150	2	8.0	3.5	1.0	10.5
*200	2	8.0	3.5	1.0	9.5
*250	2	7.8	4.0	1.0	10.0
*300	2	7.8	4.5	1.0	9.5
*400	2	7.8	4.5	1.0	9.0
*500	2	7.6	5.0	1.0	10.0
*1000	2	7.3	7.5	1.0	10.5
*1500	2	7.0	10.0	1.5	9.5
*2000	2	6.7	13.5	3.0	11.0
*2500	2	6.5	18.5	5.5	12.0
*3000	2	6.4	22.5	9.5	12.0
*4000	2	6.1	29.5	19.0	10.5
*5000	2	6.0	34.0	20.5	11.5
Soil*IP*SR[b]					
Harps*20 day					
*50	2	8.4	1.5	1.0	15.0
*100	2	8.2	1.5	1.0	12.5
*150	2	8.2	2.0	1.0	14.0
*200	2	8.2	2.0	1.0	11.5
*250	2	8.1	2.0	1.0	11.5
*300	2	8.2	2.0	1.0	12.0
*400	2	8.0	2.0	1.0	15.0
*500	2	8.0	2.0	1.0	14.0
*1000	2	8.0	2.0	1.0	14.5
*1500	2	7.8	2.5	1.0	13.0
*2000	2	7.8	3.0	1.0	14.0
*2500	2	7.8	3.5	1.5	13.5
*3000	2	7.7	3.5	1.5	13.0
*4000	2	7.7	5.5	1.5	12.5
*5000	2	7.7	5.5	2.0	13.0
*40 day*50	2	8.4	1.0	1.0	10.5
*100	2	8.3	1.0	1.0	10.5
*150	2	8.3	1.0	1.0	11.0
*200	2	8.3	1.0	1.0	10.0
*250	2	8.2	1.0	1.0	11.0

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*300	2	8.3	1.0	1.0	11.0
*400	2	8.1	1.0	1.0	11.0
*500	2	8.2	1.5	1.0	10.5
*1000	2	7.8	1.5	1.0	13.0
*1500	2	7.9	2.0	1.0	10.5
*2000	2	7.8	2.5	1.0	11.5
*2500	2	7.8	2.5	1.0	11.5
*3000	2	7.7	3.5	1.0	15.0
*4000	2	7.7	4.0	1.0	12.0
*5000	2	7.6	5.0	1.0	12.5
Storden*20 day					
*50	2	7.7	4.0	1.0	3.0
*100	2	7.5	4.0	1.0	3.0
*150	2	7.6	5.0	1.0	2.5
*200	2	7.5	4.5	1.0	2.0
*250	2	7.6	4.5	1.0	3.0
*300	2	7.5	4.5	1.0	2.5
*400	2	7.5	4.5	1.0	2.5
*500	2	7.5	4.5	1.5	2.0
*1000	2	7.4	5.5	2.0	3.0
*1500	2	7.4	6.0	3.0	2.5
*2000	2	7.3	6.5	4.5	2.5
*2500	2	7.3	6.5	16.5	3.0
*3000	2	7.1	8.0	13.0	3.5
*4000	2	7.4	8.0	16.5	2.5
*5000	2	7.4	8.5	19.5	3.5
Soil*IP*SR[b]					
Storden*40 day					
*50	2	7.7	3.0	1.0	2.5
*100	2	7.7	3.0	1.0	3.0
*150	2	7.7	3.0	1.0	3.0
*200	2	7.7	3.0	1.0	2.5
*250	2	7.8	3.0	1.0	3.0
*300	2	7.6	3.5	1.0	2.5
*400	2	7.5	3.5	1.0	2.0
*500	2	7.6	4.0	1.0	2.5
*1000	2	7.5	4.5	1.0	2.5
*1500	2	7.4	6.0	2.0	3.0
*2000	2	7.2	6.0	2.0	2.5
*2500	2	7.1	6.5	15.0	4.0
*3000	2	7.0	9.0	13.5	3.5

Table A10 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*4000	2	6.7	11.5	18.5	3.0
*5000	2	6.5	14.5	17.0	3.5
Webster*20 day					
*50	2	6.1	58.0	3.0	11.0
*100	2	6.0	58.5	3.0	10.0
*150	2	6.0	61.0	3.5	9.0
*200	2	5.9	61.5	3.5	9.5
*250	2	5.9	63.5	3.5	9.5
*300	2	5.9	64.5	3.5	8.5
*400	2	5.8	67.0	4.0	9.5
*500	2	5.8	65.0	4.5	10.5
*1000	2	5.6	74.5	10.5	9.0
*1500	2	5.6	78.0	17.5	9.0
*2000	2	5.6	81.0	22.0	10.5
*2500	2	5.5	84.0	26.5	10.5
*3000	2	5.4	88.5	30.5	9.5
*4000	2	5.4	88.0	31.0	9.0
*5000	2	5.5	93.5	35.0	10.0
Webster*40 day					
*50	2	6.0	84.0	3.0	15.0
*100	2	6.0	86.5	3.0	15.0
*150	2	5.9	89.5	3.5	13.0
*200	2	5.8	90.0	3.5	13.0
*250	2	5.7	92.5	3.5	13.0
*300	2	5.7	97.5	4.0	13.0
*400	2	5.6	101.5	4.5	14.5
*500	2	5.5	104.5	5.0	13.0
*1000	2	5.2	148.5	10.0	13.0
*1500	2	5.0	161.5	32.0	13.0
*2000	2	4.9	173.0	39.0	13.5
*2500	2	4.7	203.0	54.0	13.0
*3000	2	4.7	214.5	58.0	13.0
*4000	2	4.8	203.5	53.0	13.0
*5000	2	4.8	208.5	59.5	14.0

Table A11. pH and DTPA-extractable Fe, Mn, and Zn of calcareous soils as affected by four two-factor and four three-factor interactions

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
IP*SS					
20 day*PS	30	7.9	5.7	1.3	9.1
20 day*ES	30	7.2	6.8	5.6	8.6
40 day*PS	30	7.9	4.7	1.1	7.8
40 day*ES	30	7.1	7.8	6.0	8.5
Soil*SR[b]					
Canisteo*50	4	8.0	4.0	1.0	9.0
*100	4	8.0	4.3	1.0	8.8
*150	4	7.9	4.3	1.0	10.3
*200	4	7.9	4.3	1.0	10.3
*250	4	7.8	4.8	1.0	10.3
*300	4	7.7	5.0	1.0	9.8
*400	4	7.7	5.5	1.0	9.8
*500	4	7.5	6.0	1.0	10.3
*1000	4	7.3	8.0	1.0	10.5
*1500	4	7.0	10.3	1.5	11.3
*2000	4	6.7	13.0	3.0	10.8
*2500	4	6.6	16.3	4.5	11.5
*3000	4	6.4	19.5	7.5	11.8
*4000	4	6.2	26.3	16.3	10.5
*5000	4	6.0	30.0	19.3	11.5
Harps*50	4	8.4	1.3	1.0	12.8
*100	4	8.2	1.3	1.0	11.5
*150	4	8.2	1.5	1.0	12.5
*200	4	8.2	1.5	1.0	10.8
*250	4	8.1	1.5	1.0	11.3
*300	4	8.2	1.5	1.0	11.5
*400	4	8.1	1.5	1.0	13.0
*500	4	8.1	1.8	1.0	12.3
*1000	4	7.9	1.8	1.0	13.8
*1500	4	7.9	2.3	1.0	11.8
*2000	4	7.8	2.8	1.0	12.8
*2500	4	7.8	3.0	1.3	12.5
*3000	4	7.7	3.5	1.3	14.0
*4000	4	7.7	4.8	1.3	12.3
*5000	4	7.6	5.3	1.5	12.8

[a]IP, incubation period; SS, sulfur source; SR, sulfur rate; PS, pyrite sulfur; ES, elemental sulfur.

[b]µg S/g soil.

Table A11 (continued)

Factors	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
Storden*50	4	7.7	3.5	1.0	2.8
*100	4	7.6	3.5	1.0	3.0
*150	4	7.6	4.0	1.0	2.8
*200	4	7.6	3.8	1.0	2.3
*300	4	7.6	4.0	1.0	2.5
*400	4	7.5	4.0	1.0	2.3
*500	4	7.5	4.3	1.3	2.3
*1000	4	7.4	5.0	1.5	2.8
*1500	4	7.4	6.0	2.5	2.8
*2000	4	7.3	6.3	3.3	2.5
*2500	4	7.2	6.5	15.8	3.5
*3000	4	7.1	8.5	13.3	3.5
*4000	4	7.1	9.8	17.5	2.8
*5000	4	6.9	11.5	18.8	3.5
IP*SR[b]					
20 day*50	6	8.1	3.0	1.0	8.7
*100	6	8.0	3.2	1.0	7.7
*150	6	8.00	3.2	1.0	8.2
*200	6	8.0	3.2	1.0	7.5
*250	6	8.0	3.3	1.0	7.8
*300	6	8.0	3.5	1.0	8.0
*400	6	7.9	3.7	1.0	8.3
*500	6	8.0	3.7	1.2	8.2
*1000	6	7.9	4.7	1.2	9.3
*1500	6	7.8	5.5	1.3	8.3
*2000	6	7.8	6.0	1.3	8.3
*2500	6	7.8	6.7	1.5	9.0
*3000	6	7.8	7.8	1.5	9.3
*4000	6	7.7	9.7	1.5	9.0
*5000	6	7.7	10.8	1.7	9.3
40 day*50	6	8.0	2.8	1.0	7.7
*100	6	7.9	2.8	1.0	7.8
*150	6	7.8	3.3	1.0	8.8
*200	6	7.8	3.2	1.0	8.0
*250	6	7.7	3.3	1.0	8.5
*300	6	7.7	3.5	1.6	7.8
*400	6	7.6	3.7	1.6	8.3
*500	6	7.4	4.3	1.0	8.3
*1000	6	7.2	5.2	1.2	8.7
*1500	6	7.0	6.8	2.0	8.8

Table A11 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*2000	6	6.7	8.7	3.5	9.0
*2500	6	6.6	10.5	12.8	9.3
*3000	6	6.4	13.2	13.2	10.2
*4000	6	6.2	17.5	21.8	8.0
*5000	6	6.0	20.3	24.7	9.2
SS*SR[b]					
PS*50	6	8.1	3.0	1.0	8.7
*100	6	8.0	3.2	1.0	7.7
*150	6	8.0	3.2	1.0	8.2
*200	6	8.0	3.2	1.0	7.5
*250	6	8.0	3.3	1.0	7.8
*300	6	8.0	3.5	1.0	8.0
*400	6	7.9	3.7	1.0	8.3
*500	6	8.0	3.7	1.2	8.2
*1000	6	7.9	4.7	1.2	9.3
*1500	6	7.8	5.5	1.3	8.3
*2000	6	7.8	6.0	1.3	8.3
*2500	6	7.8	6.7	1.5	9.0
*3000	6	7.8	7.8	1.5	9.3
*4000	6	7.7	9.7	1.5	9.0
*5000	6	7.7	10.8	1.7	9.3
ES*50	6	8.0	2.8	1.0	7.6
*100	6	7.9	2.8	1.0	7.8
*150	6	7.8	3.3	1.0	8.8
*200	6	7.8	3.2	1.0	8.0
*250	6	7.7	3.3	1.0	8.5
*300	6	7.7	3.5	1.0	7.8
*400	6	7.6	3.7	1.0	8.3
*500	6	7.4	4.3	1.0	8.3
*1000	6	7.2	5.2	1.2	8.6
*1500	6	7.0	6.8	2.0	8.8
*2000	6	6.7	8.7	3.5	9.0
*2500	6	6.6	10.5	12.8	9.3
*3000	6	6.4	13.2	13.2	10.2
*4000	6	6.2	17.5	21.8	8.0
*5000	6	6.0	20.3	24.7	9.1
Soil*IP*SS					
Canisteo*20 day					
*PS	15	7.8	7.0	1.0	10.9
*ES	15	6.6	13.8	6.2	10.3

Table A11 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
Canisteo*40 day					
*PS	15	7.9	5.5	1.0	9.7
*ES	15	6.6	16.7	8.1	10.7
Harps*20 day					
*PS	15	8.2	3.4	1.3	13.4
*ES	15	7.7	2.0	1.1	13.1
*40 day*PS	15	8.2	2.7	1.0	10.8
*ES	15	7.8	1.3	1.0	12.0
Storden*20 day					
*PS	15	7.5	6.7	1.6	3.0
*ES	15	7.3	4.5	9.5	2.4
*40 day*PS	15	7.7	5.9	1.4	3.0
*ES	15	7.0	5.3	9.0	2.7
Soil*SS*SR[b]					
Canisteo*PS					
*50	2	8.1	4.0	1.0	9.5
*100	2	8.0	4.5	1.0	8.5
*150	2	8.0	4.0	1.0	10.5
*200	2	8.1	4.0	1.0	10.5
*250	2	8.0	4.5	1.0	9.5
*300	2	8.0	4.5	1.0	9.0
*400	2	8.0	5.0	1.0	9.0
*500	2	7.9	5.0	1.0	10.0
*1000	2	8.0	6.0	1.0	10.0
*1500	2	7.8	6.5	1.0	11.5
*2000	2	7.8	7.0	1.0	10.5
*2500	2	7.8	8.0	1.0	11.5
*3000	2	7.8	8.5	1.0	12.0
*4000	2	7.7	10.0	1.0	10.5
*5000	2	7.6	12.0	1.0	11.5
*ES*50	2	8.0	4.0	1.0	8.5
*100	2	8.0	4.0	1.0	9.0
*150	2	7.9	4.5	1.0	10.0
*200	2	7.8	4.5	1.0	10.0
*250	2	7.6	5.0	1.0	11.0
*300	2	7.5	5.5	1.0	10.5
*400	2	7.4	6.0	1.0	10.5
*500	2	7.1	7.0	1.0	10.5
*1000	2	6.6	10.0	1.0	11.0
*1500	2	6.2	14.0	2.0	11.0

Table A11 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			μg/g soil		
*2000	2	5.7	19.0	5.0	11.0
*2500	2	5.4	24.5	8.0	11.5
*3000	2	5.1	30.5	14.0	11.5
*4000	2	4.6	42.5	31.5	10.5
*5000	2	4.4	48.0	37.5	11.5
Harps*PS*50	2	8.5	1.5	1.0	13.5
*100	2	8.4	1.5	1.0	11.5
*150	2	8.4	1.5	1.0	11.5
*200	2	8.4	1.5	1.0	10.0
*250	2	8.4	1.5	1.0	10.5
*300	2	8.5	1.5	1.0	12.0
*400	2	8.3	1.5	1.0	13.5
*500	2	8.4	1.5	1.0	12.5
*1000	2	8.2	2.0	1.0	14.5
*1500	2	8.0	3.0	1.0	10.5
*2000	2	8.0	4.0	1.0	12.0
*2500	2	8.0	4.5	1.5	11.5
*3000	2	8.0	5.0	1.5	12.5
*4000	2	8.0	7.0	1.5	13.5
*5000	2	7.9	8.0	1.5	12.5
Soil*SS*SR[b]					
Harps*ES*50	2	8.4	1.0	1.0	12.6
*100	2	8.2	1.0	1.0	11.5
*150	2	8.1	1.5	1.0	13.5
*200	2	8.1	1.5	1.0	11.5
*250	2	7.9	1.5	1.0	12.0
*300	2	8.0	1.5	1.0	11.0
*400	2	7.9	1.5	1.0	12.5
*500	2	7.8	2.0	1.0	12.0
*1000	2	7.6	1.5	1.0	13.0
*1500	2	7.7	1.5	1.0	13.0
*2000	2	7.6	1.5	1.0	13.5
*2500	2	7.7	1.5	1.0	13.5
*3000	2	7.5	2.0	1.0	15.5
*4000	2	7.4	2.5	1.5	11.0
*5000	2	7.4	2.5	1.0	13.0
Storden*PS					
*50	2	7.7	3.5	1.0	3.0
*100	2	7.6	3.5	1.0	3.0
*150	2	7.7	4.0	1.0	2.5
*200	2	7.6	4.0	1.0	2.0

Table A11 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			μg/g soil		
*250	2	7.8	4.0	1.0	3.5
*300	2	7.6	4.5	1.0	3.0
*400	2	7.6	4.5	1.0	2.5
*500	2	7.7	4.5	1.5	2.0
*1000	2	7.6	6.0	1.5	3.5
*1500	2	7.7	7.0	2.0	3.0
*2000	2	7.6	7.0	2.0	2.5
*2500	2	7.6	7.5	2.0	4.0
*3000	2	7.6	10.0	2.0	3.5
*4000	2	7.5	12.0	2.0	3.0
*5000	2	7.5	12.5	2.5	4.0
Storden*ES					
*50	2	7.7	3.5	1.0	2.5
*100	2	7.6	3.5	1.0	3.0
*150	2	7.6	4.0	1.0	3.0
*200	2	7.6	3.5	1.0	2.5
*250	2	7.6	3.5	1.0	2.5
*300	2	7.6	3.5	1.0	2.0
*400	2	7.5	3.5	1.0	2.0
*500	2	7.4	4.0	1.0	2.5
*1000	2	7.3	4.0	1.5	2.0
*1500	2	7.1	5.0	3.0	2.5
*2000	2	7.0	5.5	4.5	2.5
*2500	2	6.7	5.5	29.5	3.0
*3000	2	6.6	7.0	24.5	3.5
*4000	2	6.6	7.5	33.0	2.5
*5000	2	6.3	10.5	35.0	3.0
IP*SS*SR[b]					
20 day*PS					
*50	3	8.0	3.7	1.0	10.0
*100	3	7.9	4.0	1.0	8.3
*150	3	7.9	4.0	1.0	8.7
*200	3	7.9	4.0	1.0	8.3
*250	3	7.9	4.0	1.0	8.0
*300	3	7.9	4.0	1.0	8.3
*400	3	7.9	4.3	1.0	9.7
*500	3	7.9	4.3	1.3	9.0
*1000	3	7.9	5.3	1.3	9.7
*1500	3	7.8	6.0	1.3	9.3
*2000	3	7.8	6.7	1.3	9.3

Table A11 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*2500	3	7.7	7.3	1.6	9.3
*3000	3	7.8	8.0	1.6	10.0
*4000	3	7.7	9.7	1.6	9.0
*5000	3	7.7	10.3	2.0	9.3
20 day*ES					
*50	3	8.0	3.3	1.0	8.3
*100	3	7.9	3.3	1.0	7.7
*150	3	7.8	4.0	1.0	9.0
*200	3	7.8	3.7	1.0	8.0
*250	3	7.6	4.0	1.0	8.7
*300	3	7.6	4.0	1.0	8.0
*400	3	7.5	4.3	1.0	9.0
*500	3	7.4	4.7	1.0	8.7
*1000	3	7.2	5.3	1.3	9.0
*1500	3	7.0	6.7	2.3	9.7
*2000	3	6.8	8.0	4.3	8.7
*2500	3	6.7	8.7	12.7	9.0
*3000	3	6.4	10.7	11.7	8.7
*4000	3	6.5	14.7	19.3	8.0
*5000	3	6.3	16.3	24.3	9.3
40 day*PS					
*50	3	8.1	2.3	1.0	7.3
*100	3	8.1	2.3	1.0	7.0
*150	3	8.1	2.3	1.0	7.7
*200	3	8.1	2.3	1.0	6.7
*250	3	8.1	2.7	1.0	7.7
*300	3	8.1	3.0	1.0	7.7
*400	3	8.0	3.0	1.0	7.0
*500	3	8.1	3.0	1.0	7.3
*1000	3	7.9	4.0	1.0	9.0
*1500	3	7.8	5.0	1.3	7.3
*2000	3	7.8	5.3	1.3	7.3
*2500	3	7.8	6.0	1.3	8.7
*3000	3	7.7	7.7	1.3	8.7
*4000	3	7.7	9.7	1.3	9.0
*5000	3	7.6	11.3	1.3	9.3
IP*SS*SR[b]					
40 day*ES					
*50	3	8.0	2.3	1.0	7.0
*100	3	7.9	2.3	1.0	8.0

Table A11 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*150	3	7.8	2.7	1.0	8.7
*200	3	7.9	2.7	1.0	8.0
*250	3	7.7	2.7	1.0	8.3
*300	3	7.7	3.0	1.0	7.7
*400	3	7.6	3.0	1.0	7.7
*500	3	7.4	4.0	1.0	8.0
*1000	3	7.1	5.0	1.0	8.3
*1500	3	7.0	7.0	1.7	8.0
*2000	3	6.7	9.3	2.7	9.3
*2500	3	6.4	12.3	13.0	9.7
*3000	3	6.3	15.7	14.7	11.7
*4000	3	5.9	20.3	24.3	8.0
*5000	3	5.7	24.3	25.0	9.0
Soil*IP*SR[b]					
Canisteo*20 day					
*50	2	8.0	5.0	1.0	9.5
*100	2	8.0	5.5	1.0	8.5
*150	2	7.9	5.0	1.0	10.0
*200	2	7.9	5.0	1.0	11.0
*250	2	7.8	5.5	1.0	10.5
*300	2	7.6	5.5	1.0	10.0
*400	2	7.6	6.5	1.0	10.5
*500	2	7.4	7.0	1.0	10.5
*1000	2	7.3	8.5	1.0	10.5
*1500	2	7.0	10.5	1.5	13.0
*2000	2	6.8	12.5	3.0	10.5
*2500	2	6.6	14.0	3.5	11.0
*3000	2	6.5	16.5	5.5	11.5
*4000	2	6.2	23.0	13.5	10.5
*5000	2	6.1	26.0	18.0	11.5
*40 day*50	2	8.1	3.0	1.0	8.5
*100	2	8.0	3.0	1.0	9.0
*150	2	8.0	3.5	1.0	10.5
*200	2	8.0	3.5	1.0	9.5
*250	2	7.8	4.0	1.0	10.0
*300	2	7.8	4.5	1.0	9.5
*400	2	7.8	4.5	1.0	9.0
*500	2	7.6	5.0	1.0	10.0
*1000	2	7.3	7.5	1.0	10.5
*1500	2	7.0	10.0	1.5	9.5

Table A11 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*2000	2	6.7	13.5	3.0	11.0
*2500	2	6.5	18.5	5.5	12.0
*3000	2	6.4	22.5	9.5	12.0
*4000	2	6.1	29.5	19.0	10.5
*5000	2	6.0	34.0	20.5	11.5
Soil*IP*SR[b]					
Harps*20 day					
*50	2	8.4	1.5	1.0	15.0
*100	2	8.2	1.5	1.0	12.5
*150	2	8.2	2.0	1.0	14.0
*200	2	8.2	2.0	1.0	11.5
*250	2	8.1	2.0	1.0	11.5
*300	2	8.2	2.0	1.0	12.0
*400	2	8.0	2.0	1.0	15.0
*500	2	8.0	2.0	1.0	14.0
*1000	2	8.0	2.0	1.0	14.5
*1500	2	7.8	2.5	1.0	13.0
*2000	2	7.8	3.0	1.0	14.0
*2500	2	7.8	3.5	1.5	13.5
*3000	2	7.7	3.5	1.5	13.0
*4000	2	7.7	5.5	1.5	12.5
*5000	2	7.7	5.5	2.0	13.0
*40 day*50	2	8.5	1.0	1.0	10.5
*100	2	8.3	1.0	1.0	10.5
*150	2	8.3	1.0	1.0	11.0
*200	2	8.3	1.0	1.0	10.0
*250	2	8.2	1.0	1.0	11.0
*300	2	8.3	1.0	1.0	11.0
*400	2	8.1	1.0	1.0	11.0
*500	2	8.2	1.5	1.0	10.5
*1000	2	7.8	1.5	1.0	13.0
*1500	2	7.9	2.0	1.0	10.5
*2000	2	7.8	2.5	1.0	11.5
*2500	2	7.8	2.5	1.0	11.5
*3000	2	7.7	3.5	1.0	15.0
*4000	2	7.7	4.0	1.0	12.0
*5000	2	7.6	5.0	1.0	12.5
Storden*20 day					
*50	2	7.7	4.0	1.0	3.0
*100	2	7.5	4.0	1.0	3.0

Table A11 (continued)

Factors[a]	No. of obsns	pH	Fe	Mn	Zn
			µg/g soil		
*150	2	7.6	5.0	1.0	2.5
*200	2	7.5	4.5	1.0	2.0
*250	2	7.6	4.5	1.0	3.0
*300	2	7.5	4.5	1.0	2.5
*400	2	7.5	4.5	1.0	2.5
*500	2	7.5	4.5	1.5	2.0
*1000	2	7.4	5.5	2.0	3.0
*1500	2	7.4	6.0	3.0	2.5
*2000	2	7.3	6.5	4.5	2.5
*2500	2	7.3	6.5	16.5	3.0
*3000	2	7.1	8.0	13.0	3.5
*4000	2	7.4	8.0	16.5	2.5
*5000	2	7.4	8.5	19.5	3.5
Soil*IP*SR[b]					
Storden*40 day					
*50	2	7.7	3.0	1.0	2.5
*100	2	7.7	3.0	1.0	3.0
*150	2	7.7	3.0	1.0	3.0
*200	2	7.7	3.0	1.0	2.5
*250	2	7.8	3.0	1.0	3.0
*300	2	7.6	3.5	1.0	2.5
*400	2	7.5	3.5	1.0	2.0
*500	2	7.6	4.0	1.0	2.5
*1000	2	7.5	4.5	1.0	2.5
*1500	2	7.4	6.0	2.0	3.0
*2000	2	7.2	6.0	2.0	2.5
*2500	2	7.1	6.5	15.0	4.0
*3000	2	7.0	9.0	13.5	3.5
*4000	2	6.7	11.5	18.5	3.0
*5000	2	6.5	14.5	18.0	3.5

Table A12. Comparison of predicted extractable Fe developed from the selected regression model for each S source and observed Fe values at two incubation periods and 15 S rates for Canisteo soil

S rate	S source							
	Elemental S[a]				Pyrite[b]			
	20 day		40 day		20 day		40 day	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
μ S/g soil	μg Fe/g soil							
50	5.1	5.3	3.2	6.3	5.1	4.1	3.2	4.5
100	5.2	5.4	3.4	6.4	6.2	4.1	3.3	4.5
150	5.2	5.5	3.7	6.5	5.3	4.2	3.3	4.6
200	5.3	5.7	3.7	6.7	5.2	4.2	3.3	4.6
250	5.8	5.8	4.5	6.8	5.5	4.3	3.6	4.7
300	6.2	5.9	5.0	7.0	5.4	4.3	3.5	4.7
400	6.8	6.1	4.8	7.3	5.6	4.4	3.6	4.8
500	7.6	6.4	6.2	7.6	5.8	4.5	4.1	4.9
1000	10.0	7.9	10.0	9.3	6.5	5.1	4.5	5.5
1500	13.3	9.7	14.8	11.5	8.0	5.6	5.2	6.1
2000	17.3	12.0	21.3	14.2	8.0	6.3	5.9	6.9
2500	19.4	14.8	29.9	17.5	9.4	7.0	7.1	7.6
3000	24.4	18.3	37.5	21.6	9.4	7.8	7.8	8.5
4000	36.1	27.8	48.9	32.9	10.2	9.8	10.0	10.6
5000	41.1	42.3	54.9	50.0	11.5	12.2	12.9	13.2

[a] $R^2 = 0.965$ for regression model.

[b] $R^2 = 0.971$ for regression model.

Table A13. Comparison of predicted extractable Fe developed from the selected regression model for each S source and observed Fe values at two incubation periods and 15 S rates for Harps soil

S rate	S source							
	Elemental S[a]				Pyrite[b]			
	20 day		40 day		20 day		40 day	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
µg S/g soil	µg Fe/g soil							
50	1.5	1.4	0.9	0.9	1.7	1.7	0.9	1.1
100	1.5	1.4	0.9	0.9	1.5	1.8	1.0	1.1
150	1.6	1.5	1.4	0.9	1.5	1.8	0.8	1.1
200	1.8	1.5	1.8	0.9	2.0	1.9	1.0	1.2
250	1.8	1.5	1.1	0.9	1.6	1.9	1.0	1.2
300	1.9	1.5	1.0	0.9	1.7	1.9	1.1	1.2
400	1.7	1.5	1.1	0.9	2.0	2.0	1.2	1.3
500	1.9	1.6	1.6	1.0	2.1	2.1	1.3	1.3
1000	1.9	1.8	1.4	1.1	2.5	2.6	2.4	1.6
1500	2.2	2.0	1.2	1.2	3.5	3.2	3.0	2.0
2000	2.1	2.2	1.4	1.4	4.6	3.9	3.9	2.4
2500	2.2	2.5	1.4	1.5	4.8	4.8	4.5	3.0
3000	2.4	2.9	1.8	1.7	5.5	5.9	5.2	3.7
4000	2.8	3.6	2.0	2.2	7.5	8.9	5.9	5.5
5000	3.2	4.6	2.2	2.8	8.5	13.4	7.5	8.4

[a] R^2 = 0.965 for regression model.

[b] R^2 = 0.971 for regression model.

Table A14. Comparison of predicted extractable Fe developed from the selected regression model for each S source and observed Fe values at two incubation periods and 15 S rates for Storden soil

S rate	S source							
	Elemental S[a]				Pyrite[b]			
	20 day		40 day		20 day		40 day	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
µg S/g soil	µg Fe/g soil							
50	4.3	3.9	3.1	4.2	4.0	4.1	3.3	4.1
100	4.3	4.0	3.2	4.3	4.3	4.1	3.2	4.1
150	4.5	4.0	3.0	4.3	4.6	4.2	3.1	4.2
200	4.3	4.0	2.8	4.3	5.1	4.2	3.5	4.2
250	4.4	4.0	2.8	4.3	4.6	4.3	3.2	4.3
300	4.3	4.0	3.3	4.3	5.2	4.3	3.8	4.3
400	4.3	4.0	3.3	4.4	5.0	4.4	4.0	4.5
500	4.3	4.1	3.6	4.4	5.1	4.5	3.8	4.6
1000	4.4	4.2	4.2	4.6	6.8	5.1	4.7	5.2
1500	4.9	4.4	4.6	4.7	6.9	5.8	7.0	5.8
2000	5.0	4.6	5.8	4.9	8.4	6.6	6.2	6.6
2500	5.3	4.8	6.4	5.1	8.5	7.4	7.5	7.5
3000	6.5	5.0	8.3	5.3	9.6	8.4	9.9	8.5
4000	4.7	5.4	10.4	5.8	11.0	10.7	13.4	10.8
5000	4.8	5.8	15.8	6.2	12.3	10.7	13.4	13.8

[a] R^2 = 0.965 for regression model.

[b] R^2 = 0.971 for regression model.

Table A15. Comparison of predicted extractable Fe developed from the selected regression model for each S source and observed Fe values at two incubation periods and 15 S rates for Webster soil

S rate	S source							
	Elemental S[a]				Pyrite[b]			
	20 day		40 day		20 day		40 day	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
µg S/g soil	µg Fe/g soil							
50	56.9	56.5	82.1	70.0	59.1	71.1	85.8	80.5
100	57.7	57.3	85.7	70.9	59.5	71.8	87.0	81.3
150	61.6	58.1	91.0	71.9	60.0	72.6	87.7	82.2
200	62.6	58.9	94.0	72.9	60.3	73.3	86.5	83.0
250	62.7	59.7	93.1	73.9	63.6	74.1	91.7	83.9
300	65.1	60.5	99.1	74.9	64.2	74.8	96.0	84.7
400	63.8	62.2	99.4	77.0	69.7	76.4	104.0	86.5
500	62.9	63.9	101.6	79.1	66.9	78.0	106.4	88.3
1000	77.5	73.3	118.8	90.8	71.6	86.4	178.4	97.9
1500	79.5	84.1	129.2	104.1	76.1	95.8	194.3	108.5
2000	82.9	96.4	142.0	119.5	78.7	105.5	203.1	120.3
2500	83.7	110.7	158.2	137.0	84.3	117.7	248.5	133.3
3000	90.0	126.9	165.7	158.2	87.2	130.5	262.5	147.8
4000	89.4	167.0	151.7	206.8	87.4	160.3	254.8	181.6
5000	99.0	219.7	163.6	272.1	87.4	197.0	253.4	223.1

[a] R^2 = 0.965 for regression model.

[b] R^2 = 0.971 for regression model.

Table A16. Comparison of predicted extractable Mn developed from the selected regression model for each S source and observed Mn values at two incubation periods and 15 S rates for Canisteo soil

S rate	S source							
	Elemental S[a]				Pyrite[b]			
	20 day		40 day		20 day		40 day	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
µg S/g soil	µg Fe/g soil							
50	0.7	0.7	0.5	1.2	0.7	1.0	0.6	1.0
100	0.6	0.8	0.6	2.0	0.7	1.0	0.5	1.0
150	0.7	0.8	0.6	2.1	0.6	1.0	0.6	1.0
200	0.6	0.8	0.6	3.3	0.7	1.0	0.6	1.0
250	0.6	0.8	0.6	3.5	0.7	1.0	0.6	1.0
300	0.6	0.8	0.7	5.3	0.6	1.0	0.6	1.0
400	0.7	0.8	0.5	5.8	0.7	1.0	0.6	1.0
500	0.8	0.9	0.7	8.2	0.7	1.0	0.8	1.0
1000	1.1	0.9	1.1	8.7	0.8	1.0	0.6	1.0
1500	2.1	0.9	2.0	12.1	0.8	1.0	0.7	1.0
2000	4.6	0.9	4.7	12.8	0.7	1.0	0.7	1.0
2500	6.0	1.0	9.8	21.8	0.8	1.0	0.8	1.0
3000	10.1	1.1	17.5	23.0	0.9	1.0	0.8	1.0
4000	25.7	1.1	37.1	28.3	0.9	1.0	0.8	1.0
5000	35.1	1.2	40.3	29.9	11.0	1.0	0.8	1.0

[a] R^2 = 0.931 for regression model.

[b] R^2 = 0.909 for regression model.

Table A17. Comparison of predicted extractable Mn developed from the selected regression model for each S source and observed Mn values at two incubation periods and 15 S rates for Harps soil

S rate	S source							
	Elemental S[a]				Pyrite[b]			
	20 day		40 day		20 day		40 day	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
µg S/g soil	µg Mn/g soil							
50	1.2	0.8	1.1	1.0	1.4	1.0	1.1	1.0
100	1.1	0.9	1.1	1.1	1.1	1.0	1.2	1.1
150	1.1	0.8	1.0	1.1	1.1	1.0	1.0	1.0
200	1.1	0.9	1.1	1.2	1.2	1.0	1.0	1.1
250	1.0	0.8	0.9	1.3	1.1	1.0	1.1	1.1
300	1.0	0.9	0.9	1.3	1.1	0.9	1.1	1.2
400	0.4	0.9	0.9	1.4	1.1	1.0	1.1	1.1
500	0.8	0.9	0.9	1.4	1.2	0.9	1.2	1.3
1000	0.9	0.9	0.8	1.5	1.3	1.0	1.3	1.2
1500	0.9	0.9	0.9	1.4	1.3	0.9	1.3	1.4
2000	0.9	0.9	0.8	1.5	1.5	1.0	1.4	1.3
2500	1.1	0.9	0.9	1.2	1.6	0.9	1.4	1.5
3000	1.1	0.9	0.8	1.2	1.6	1.0	1.4	1.4
4000	1.3	1.0	0.9	0.7	1.8	1.0	1.4	1.7
5000	1.5	0.9	1.0	0.7	1.7	1.0	1.4	1.6

[a] R^2 = 0.931 for regression model.

[b] R^2 = 0.909 for regression model.

Table A18. Comparison of predicted extractable Mn developed from the selected regression model for each S source and observed Mn values at two incubation periods and 15 S rates for Storden soil

S rate	S source							
	Elemental S[a]				Pyrite[b]			
	20 day		40 day		20 day		40 day	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
µg S/g soil	µg Mn/g soil							
50	1.2	0.8	1.1	1.4	1.2	1.1	1.2	1.1
100	1.1	0.9	1.0	1.5	1.5	1.0	1.1	1.3
150	1.1	0.9	0.9	2.3	1.3	1.1	1.1	1.3
200	1.1	0.9	1.0	2.5	1.4	1.0	1.2	1.4
250	1.1	0.9	1.0	3.8	1.4	1.1	1.3	1.4
300	1.2	1.0	1.0	4.1	1.5	1.1	1.2	1.6
400	1.2	1.0	1.0	6.2	1.4	1.1	1.3	1.5
500	1.2	1.1	1.1	6.5	1.5	1.1	1.4	1.8
1000	1.5	1.1	1.1	9.5	1.5	1.1	1.3	1.7
1500	4.1	1.1	1.8	10.1	1.6	1.1	2.4	2.0
2000	7.0	1.1	2.0	14.7	1.8	1.2	1.5	1.9
2500	31.2	1.2	27.9	24.8	2.0	1.1	1.7	2.4
3000	23.5	1.2	25.0	26.2	2.1	1.2	1.9	2.3
4000	30.6	1.3	35.0	31.9	2.5	1.1	2.2	3.0
5000	36.3	1.4	34.4	33.7	2.8	1.2	2.3	2.8

[a] R^2 = 0.931 for regression model.

[b] R^2 = 0.909 for regression model.

Table A19. Comparison of predicted extractable Mn developed from the selected regression model for each S source and observed Mn values of two incubation periods and 15 S rates for Webster soil

S rate	S source							
	Elemental S[a]				Pyrite[b]			
	20 day		40 day		20 day		40 day	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
µg S/g soil	µg Mn/g soil							
50	2.6	3.6	2.6	6.4	2.9	3.2	2.8	3.1
100	3.1	3.8	3.2	10.7	2.6	3.0	3.0	3.5
150	3.7	3.8	3.5	11.3	2.7	3.2	2.8	3.3
200	3.6	4.0	3.8	18.6	2.7	3.0	2.7	3.7
250	3.9	4.0	3.8	19.7	2.6	3.2	2.7	3.4
300	4.3	4.3	5.4	31.3	2.8	3.1	2.7	3.8
400	5.1	4.3	5.0	33.1	3.0	3.3	2.9	3.6
500	5.9	4.5	6.7	50.7	2.8	3.1	2.9	4.0
1000	18.0	4.5	32.4	53.5	3.2	3.3	3.6	3.8
1500	32.0	4.8	59.9	77.9	3.6	3.1	3.6	4.2
2000	40.5	4.8	83.0	82.3	3.8	3.3	3.9	4.0
2500	49.1	5.1	103.5	152.0	4.0	3.1	4.7	4.6
3000	57.5	5.4	110.9	160.6	4.2	3.3	4.8	4.3
4000	57.4	5.7	100.7	214.7	4.8	3.1	5.1	5.0
5000	65.1	6.1	114.1	226.9	5.1	3.3	5.4	4.7

[a] R^2 = 0.931 for regression model.

[b] R^2 = 0.909 for regression model.

Table A20. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by seven S treatments

Sulfur treatment		DM[a] yield	Leaf tissue concentration					
Source[b]	Rate		P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
C	0	2.4	0.31	1.62	0.13	108	56	38
ES	25	3.1**	0.36**	1.65	0.20**	119	71**	34
ES	50	2.8**	0.39**	1.77	0.20**	119	72**	34
ES	75	2.9**	0.37**	1.71	0.21**	118	79**	44
PS	50	2.8**	0.35**	1.72	0.19**	113	62**	38
PS	100	2.7**	0.38**	1.73	0.18**	121	69**	34
PS	150	2.9**	0.36**	1.67	0.20**	124	69**	42

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

**Significantly different from the control at 1% level.

Table A21. Dry matter yield and leaf analyses of Wayne soybean as affected by seven S treatments on four soils

Sulfur treatment		DM[a] yield	Leaf tissue concentration					
Source[b]	Rate		P	K	S	Fe	Mn	Zn
	µg S/g soil	g/pot	%			µg/g		
			Canisteo 1					
C	0	1.8	0.29	1.65	0.17	87	37	44
ES	25	3.0*	0.30	1.60	0.19	88	41	39
ES	50	2.2*	0.33	1.79	0.18	98	43	41
ES	75	2.6*	0.31	1.65	0.19	92	42	34
PS	50	2.7*	0.28	1.63	0.17	93	41	33
PS	100	2.3*	0.34	1.81	0.15	101	42	40
PS	150	2.5*	0.34	1.64	0.19	138	42	42
			Harps 1					
C	0	2.0	0.37	1.28	0.17	119	74	36
ES	25	2.8	0.37	1.18	0.15	129	97**	29
ES	50	2.3	0.43	1.34	0.18	114	97**	30
ES	75	2.2	0.42	1.27	0.19	118	106**	39
PS	50	2.6	0.38	1.34	0.21	109	79**	36
PS	100	2.1	0.46	1.41	0.22	118	97**	31
PS	150	2.7	0.38	1.15	0.18	98	112**	43
			Storden sl					
C	0	3.1	0.31	1.69	0.10	112	58	27
ES	25	3.3	0.35*	1.85	0.23**	123	77*	23
ES	50	3.6	0.37*	1.99	0.21**	134	86*	29
ES	75	3.5	0.37*	1.93	0.21**	140	95*	48
PS	50	2.9	0.37*	1.87	0.17**	131	69*	26
PS	100	3.3	0.37*	1.78	0.18**	150	80*	27
PS	150	3.8	0.36*	1.90	0.21**	143	65*	41
			Webster 1					
C	0	2.5	0.30	1.86	0.11	114	54	45
ES	25	3.2	0.39*	1.97	0.23**	136	70	45
ES	50	2.9	0.41*	1.97	0.21**	132	64	37
ES	75	3.3	0.37*	1.98	0.23**	121	73	58
PS	50	2.8	0.38*	2.02	0.21**	118	59	55
PS	100	3.2	0.36*	1.92	0.18**	114	57	39
PS	150	2.8	0.34*	2.02	0.23**	114	57	42

[a]DM, dry matter.

[b]C, control; ES, elemental S; PS, pyrite S.

*,**Significantly different from the control at the 5% and 1% level, respectively.

Table A22. Dry matter yield and leaf tissue analyses of Wayne soybean as affected by four soils at two temperatures

Soil type		DM[a] yield	Leaf tissue concentration					
			P	K	S	Fe	Mn	Zn
		g/pot	%			µg/g		
25°C								
Canisteo 1		2.4	0.31	1.61	0.16	100	40	39
Harps 1		2.4	0.39	1.22	0.16	127	95	40
Storden sl		3.1	0.37	1.92	0.21	132	79	37
Webster 1		3.0	0.34	1.87	0.21	113	59	42
Statistical evaluation[b]	1	**	ns	**	**	ns	ns	ns
	2	ns	**	**	ns	**	**	ns
	3	ns	ns	ns	ns	*	**	ns
30°C								
Canisteo 1		2.4	0.32	1.75	0.20	99	42	39
Harps 1		2.3	0.41	1.34	0.22	103	94	30
Storden sl		3.6	0.35	1.80	0.17	135	72	26
Webster 1		2.9	0.38	2.05	0.20	129	64	50
Statistical evaluation	1	**	ns	**	*	**	ns	ns
	2	ns	**	**	ns	ns	**	ns
	3	**	ns	**	ns	ns	ns	**

[a]DM, dry matter.

[b]Statistical evaluation based on the following orthogonal comparisons:

1 Canisteo 1 and Harps 1 vs Storden sl and Webster 1
2 Canisteo 1 vs Harps 1
3 Storden sl vs Webster 1.

*,**Significantly different at the 5% and 1% level, respectively; ns, not significant.

Table A23. Dry matter yield and leaf tissue analyses of Wayne soybean as influenced by soil-applied pyrite in a Harps soil

Pyrite rate	DM[a] yield	Leaf tissue concentration					
		P	K	S	Fe	Mn	Zn
µg S/g soil	g/pot	%			µg/g		
0	2.0	0.37	1.28	0.17	120	74	36
200	2.2	0.44	1.33	0.20**	131	94	29
400	2.6	0.36	1.22	0.24**	134	90	37
600	2.4	0.39	1.29	0.25**	125	91	43
800	2.8	0.43	1.25	0.21**	87	101	27
1000	2.6	0.41	1.23	0.21**	129	90	37

[a]DM, dry matter.

**Significantly different from the control at the 1% level.